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Goddard Space Flight Center

1971 NASA/Goddard-Aerospace Industry

Battery Workshop

Greenbelt, Maryland

17 November 1971

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Greenbelt, Maryland

1971 NASA/Goddard-Aerospace Industry

Battery Workshop

Chairman - Gerald Halpert

Room 231, Building 7,
Goddard Space Flight Center,
Greenbelt, Maryland.

Wednesday, 17 November 1971.

The meeting was called to order at 9:15 a.m.

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P R O C E E D I N G S

HALPERT: I would like to welcome you all to Goddard Space Flight Center for the 1971 NASA/Goddard-Aerospace Industry Battery Workshop, devoted particularly to nickel-cadmium batteries.

We moved into this more intimate room this year because we felt as though we would have a small representation from industry and government, considering the problems in business. Instead, we find that we have more people this year than we did last year. So that's either an indication that we have more problems in batteries or more people interested in batteries, and probably a combination of both.

We have sent out a tentative agenda, which I'm sure most of you should have received. I'll have some additional copies a little bit later.

You may note that our schedule is very flexible, and the purpose in doing that is to spark participation by all, or as many as we can, in discussions of the various subject matters. We can make it a real workshop by having everybody participate. If you have any information about a particular subject we would like you to feel free to take part It in turn may bring up other questions or points of interest. In this way we can keep the workshop rolling smoothly.

We do have a few planned papers of fairly short duration which will kind of introduce each of the subject areas.

The subject matter for this morning, which will be chaired by Tom Hennigan, will be separators.

I would like to introduce Tom Hennigan up here in the front row.

(Mr. Hennigan standing.)

Tom will have a session on separators, and then on seals, anticipating that that will work our way toward lunch.

In the afternoon, Floyd Ford will be the session chairman.

(Mr. Ford standing.)

His subject matter will be cell performance and specification experience.

Tomorrow morning we will be talking about materials and pre-charge, and I will be the chairman at that session.

And in the afternoon we will be talking about thermal problems and other aspects of nickel-cadmium batteries that the attendees care to discuss, and Dean Maurer, from Bell Labs, will be the chairman at that session.

Anyone who feels they will have something to say, who has not contacted one of the session chairmen, we would appreciate if you would do so, so that he knows to call on you at the particular time.

Also, if you have slides of a particular variety, 35mm or lantern type, we would like to know that ahead of time, because we have both types of projectors available and it would take some minor setting-up time ahead of time.

We have also available down here in front an opaque projector. If you have some data that you want to discuss, you can prepare your own data and show it right here on the opaque. If you have some vu-graphs, we can use the vu-graph projector.

Gene Stroup is here, in the back.

(Mr. Stroup standing.)

Gene is going to handle all of the changes in addresses. If you have a change in address for mailing, if you're not receiving literature and would like to, Gene will get your name and address and put it on our computer listing.

So if you have any corrections or changes, please see Gene, or contact him at Code 761.

Also, I will have a sign-in sheet a little later. This sign-in sheet is important for our recorder to have, so that when Mr. Bloom is recording what you have to say, recording your name, he will have the correct name and address to work from. So we will send around a name listing.

We're very pleased to have some foreign visitors with us this morning.

From Canada, several persons, who or whom we're very happy to have with us. . Joe Lackner and Ron Haines of the Defense Research Establishment.

(Mr. Lackner and Mr. Haines standing.)

That is D-R-E, Defense Research Establishment. I want to get that straight for the record.

We have from the Canadian Department of Communication, George Mackie.

(Mr. Mackie standing.)

And from Telesat Canada, Ed Hendee and Mike Stott.

(Mr. Hendee and Mr. Stott standing.)

From Leigh Instruments of Ottawa, Nicholas Balke.

(Mr. Balke standing.)

And from SAFT, France, Silvio Font.

(Mr. Font standing.)

We're very happy to have all of you with us this morning, in addition to all of our American friends, to try to understand some of the problems we're having with nickel-cadmium batteries.

I do want to tell you a little bit about the ground rules for our workshop. Mr. Bill Bloom from Ace-Federal Reporters is sitting here to my left. He is going to record verbatim what we will be discussing. There is some minor editing done, mainly to remove the coughs and the laughter expressions in the paper, but all the entire proceedings will be produced in a document at the end of the session; which we hope to have to you within the space of a month.

There are some additional copies of last year's sessions. And if you were not here and would like to get a copy, they are in the back of the room.

When you are speaking, if you have a prepared paper, we would appreciate your giving the title of the paper, your name and company. And if you have questions from the floor, would you please identify yourself by name and company, carefully, so we can have it recorded properly.

We have three microphones -- two in addition to this one -- around the room. And hopefully the extension cords are long enough so that we can pass them around, so that everyone will have the possibility of speaking if they desire to.

We will print, as we did last year, all copies of photographs and data, and vu-graphs. So if you are using visual material, we would appreciate having copies as soon after the meeting as possible, so that we can include them in the notes. We found that this worked out very well last year, and hope that it will work out this year.

We intend to have a couple of coffee breaks each day, one in the morning and one in the afternoon. And we will try and break promptly at noon for lunch. The cafeteria at Goddard is expecting us, and either Tom or I will give you directions on how to get over there at that time.

If you have a problem with travel arrangements, our travel office is available, and any one of our chairmen would be very happy to get you to a phone to contact the proper people for your reservations and information.

We hope possibly to have, during one of our breaks, a short tour of this building, which you may find very interesting.

We have a catwalk over here that runs along the building that covers the test and evaluation area for satellites. We're not sure exactly how that is going to be planned in, but we hope to arrange it.

Also, there is a museum of all of the old Goddard satellites in one of the other buildings. And if we can fit it in, we hope to have a walk-through of that museum.

There are some displays and there will be some added displays set up, and there are some extra copies of documents that have been produced in the past around the room, and during the breaks if you desire you can take a look at what is available. There are several from Goddard, as I said, there are several copies of reports, and there are also copies of last year's minutes of the meeting.

Well, that's all I have at this particular time.

Is there any question about the ground rules or about how we are going to work the meeting? Any problems we can ask about at this time?

(No response)

Okay. Then I would like to introduce our first chairman for this morning, Tom Hennigan from Goddard Space Flight Center.

wb1

HENNIGAN: Thank you very much, Gerry.

I would also like very much to welcome everyone here this morning to Goddard Space Flight Center. I guess this is our fourth workshop meeting of this type, if we don't count the one we had at Edison a few years ago.

And I would also like to emphasize again the purpose of the meeting is to get people to discuss their problems, their results. And that's beneficial to everybody.

I just would like to say something about the spec. You know we all wrote a spec some years ago, the Goddard-Industry Committee on process and material control over ni-cad batteries. And without going on too much about this, it had to be reduced somewhat to a practical spec; which worked out fairly well.

As far as we can tell right now, most space programs use this spec, all programs use at least parts of it. The battery companies have come around to accepting the spec. And the cost of the cells with the spec is about a hundred dollars per cell extra. So it wasn't the five times the cost that people initially said it would go up to.

Of course that was with the initial spec. We've had to back off from that one.

One thing I probably should bring up: when the meeting is going on,if there is anything you don't want to record, or have recorded, just tell the fellow to shut it off.

wb2]

But don't forget to turn him back on when you're finished.

Off the record.

(Discussion off the record.)

HENNIGAN: Now let's get onto the separator area.

I guess for some years we've been trying to get a better separator for ni-cad batteries in particular. Although the nylons have served their purpose, it doesn't seem to be a long-lasting separator. Especially if we work around 25°C and 40°C, the cells fail within a year. If you can run the battery at 0°C you can live with nylon. But that's not normally the case.

You have to give the spacecraft guys a tolerance, and we're trying to shoot for zero to 25°C. I think we've convinced most people not to go to 40°C. any more, except for very short periods.

Now I think the main thing in the ni-cad area has been to find a polyprophylene material which everybody feels, or thinks, or has data that will last longer than nylon, but has the same good properties that nylon has in the cell. I guess there are about six or seven different polyprophylenes going around these days, and people have test data, and we would appreciate to hear from you this morning. I guess about four or five people have volunteered to give us some information, including myself.

So if Bob Steinhauer is ready Bob Steinhauer from

wb3

Hughes Aircraft, he has a short presentation on some scanning calorimeter work on separators.

STEINHAUER: Good morning.

Just a few comments. In our low earth orbit program that we're doing for Wright-Pat, we're using 50-ampere-hour ni-cad cells, of which we have evaluated several from different manufacturers. But the point that Tom just brought out is that where you are using a large size cell especially, where is the limitation in the separator? And we were particularly concerned with heat, and where would nylon separators degrade?

We ran a differential thermal analysis trying to simulate cell conditions, which means a flow of oxygen with some 32 percent potassium hydroxide solution, along with, in this case, Pellon 2505 material. And I would like to show this curve.

(Slide 1.)

These correspond to zero, 10, 20, and so forth, in degrees C. We ran similar curves for polyprops, and there is no problem there on out.

We're particularly concerned with exotherm starts, namely the hydrolysis reaction with the nylon. As you can see, they've labeled it as 36°C., which is pretty close to 95°F. It's just a question of whether it's 35 or 36, but it's right around in that point.

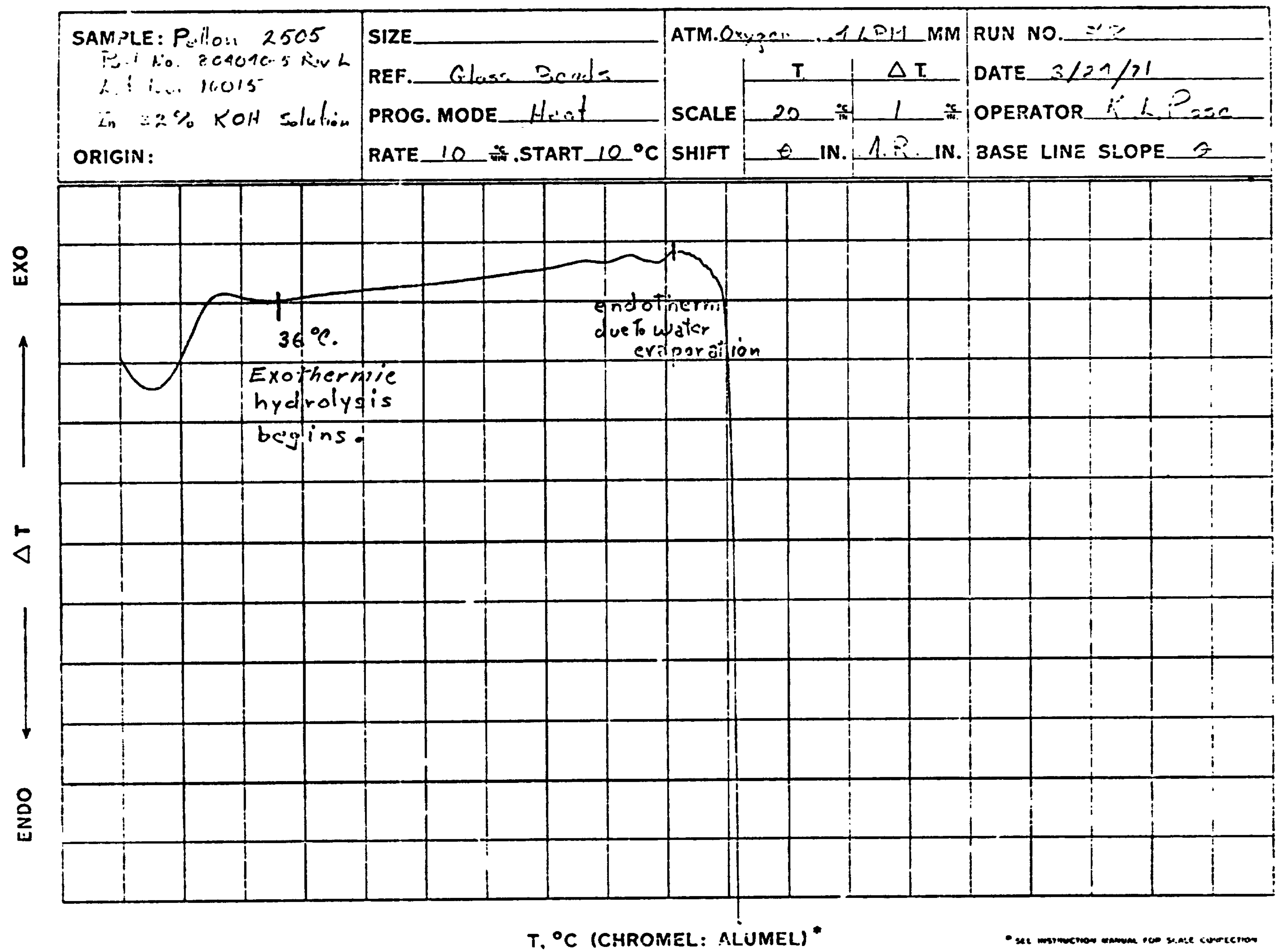

SAMPLE: Pellon 2505
ORIGIN:
SIZE
REF. Glass Beads
PROG. MODE Heat
RATE 10 °C/min START 10 °C
ATM. Oxygen MM
T
ΔT
SCALE 20 1
SHIFT 0 IN. IN.
RUN NO.
DATE 3/21/71
OPERATOR
BASE LINE SLOPE
EXO
ΔT
ENDO
36 °C.
Exothermic hydrolysis begins.
endotherm due to water evaporation
T, °C (CHROMEL: ALUMEL)*
* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

Figure 1

wb4

The concern was the large sized cells on this particular program. But this has other implications, namely if you want the center cell of your battery pack, to keep the electrolyte temperature below this point, you have to consider your spacecraft shelf temperature on that particular satellite, and then back off from that, so that that center cell is not going to reach this point.

We felt that this would give us a reasonable definition. We knew that the nylon would hydrolize; the question was where, and where did it affect us on this low earth orbit program with the large size cells.

The other point that I wanted to make is that we have indeed operated cells with the polypropylene separators in them in 50-ampere-hour size, and we have not incurred any of the pressure problems or some of the other problems that people had been concerned about with polyprop.

Thanks.

HENNIGAN: Are there any questions?

Did you mention what polypropylene you had?

STEINHAUER: We measured six different types, and all the curves by this analysis came out just about the same. There's no problem until way on out. There is no hydrolysis reaction as such.

HENNIGAN: What I meant was, was it GAF or Pellon?

wb5

STEINHAUER: I guess I don't understand....

HENNIGAN: Who made the material?

STEINHAUER: We had materials from Kendall, from Pellon, from GAF, and one or two other sources. We did not evaluate Hercules.

HENNIGAN: Are there any other questions?

I guess the next speaker on separators who has asked to talk is Mr. Gandel from Lockheed.

GANDEL: Thank you, Tom.

The title of this paper -- I will honor it with that: I've got three sheets in front of me -- is Accelerated Life Cycle Testing.

At Lockheed we've been doing a lot of work with about a 45-ampere-hour nickel-cadmium battery cell. And in fact we currently have that battery in flight.

The work that has been done so far, or the actual batteries we've built are based upon the Pellon separation.

In order to improve the long-life characteristics we decided to investigate polypropylene, and in conjunction with Eagle Picher we have been doing these investigations for about the last year and a half.

Eagle Picher had evaluated the available polypropylene separators, and based on some of that earlier work we decided to design a simple experiment based on two of the best polypropylenes and using the Pellon as a standard.

wb6

In order to accelerate this testing as fast as we felt was safe, we went to twice the cyclic rate; that is, the normal sixteen 90-minute orbits per day were adapted to 32 45-minute cycles per day, with about 22 minutes of discharge and 23 minutes of charge.

There were sixteen cells constructed, either with Pellon, eight with polypropylene. The two Pellons built into the cells were the Pellon 2505, which was compressed to a nominal 10 to 12 mils. The next group of four cells was with the 2506 Pellon compressed to 8 mils.

Where we used different separator thicknesses we adjusted the thickness of the cell, so that we at least thought we maintained the same compression.

And these cells contained nineteen positives and twenty negatives.

The Pèllon received no special treatment, as opposed to in the polypropylene we subjected that separation to three wash cycles with ethanol and three with water.

The polypropylenes built into the cells were first the WEX 124R by GAF, and that was in the 10 to 12 mil thickness. The other polypropylene was FT 2140 by Pellon, and that was 8 mil material. Both of the polypropylenes received the same wash treatment.

The results to date are-- Well, first off, on the nominal 45-ampere-hour cells, on checking capacities under the

wb7

charge-discharge regimen, all of these cells fell within the 45-to-52-ampere-hour range.

The specific discharge characteristics were under a 10 percent depth of discharge -- that is, half the cells were under a 10 percent depth of discharge, half at 20 percent depth of discharge. The rates were 12.3 amps discharge and 13.2 amps charge on the 10 percent depth of discharge, and twice those rates on the 20 percent depth of discharge.

The end of charge voltages-- If I may digress: the test is being conducted in a 50° temperature chamber, so that the max temperature on the 20 percent depth of discharge where we have a charge rate of 26.4 amps goes up to about 62°F. So for the total experiment the temperature range is between 50 and 62°F.

The end of charge voltages with the 10 percent depth of dischrage, or the 13 amp charge rate, falls in the 1.44 to 1.46 volt range. And then when we go to the 26.4 amp charge, which is nominally a C/2 rate, we end the charge at 1.46 to 1.50.

As of this date we have 3400 cycles, and the plan is to continue until failure. And there is no evidence of failure on any of the cells yet.

Are there any questions?

HENNIGAN: Thank you.

That number you have, 124R-- The people from GAF

wb8

here, is that your number? 1242: okay.

I think I'll go through the area that we've been testing for the last year now.

We gave some data on this at the meeting last year, and we were just getting started and all we had was some characteristic data on the materials themselves. But at this time we're up to about 4000 cycles on the cells that are still going.

Let me just real quickly go into how we're testing these cells.

We're testing at 20°C. They are 6-ampere-hour cells, and there are six cells in each pack, except for one set, which is Hercules, where we have eight cells.

It's a 25 percent depth of discharge, and a 90-minute orbit.

We try to maintain the charge rate at 120 percent, but we couldn't do that. So we had to back off. And I'll go into that later.

The requirement is that none of the cells can go over 155; if they do, shut them off. Or they should not go over 80 pounds gauge.

On every 1500 cycles, and we've done this twice now, we've taken out one cell for analysis of the separator.

Presently we have six packs at 4000 cycles and one pack at 2500 cycles, and three packs have failed before vb9

a thousand cycles.

BRIGGS: Briggs, Philco-Ford. You say three packs failed. How did they fail?

HENNIGAN: Very high voltages, pressure, and shorts. They just weren't very good at all.

Now in this first one, it shows you one set of separators. I want to make sure it's understood that we picked these separators as separators that would not work. I'm sure the company can make separators that will work, but these were some that were selected that would not work; that we didn't think would work, and they didn't.

(Slide 2.)

I don't know how many of you remember this chart from last year, but it shows the separators from Kendall. All the "E" separators are from Kendall.

The reason we didn't think they would work was because of the high A/C resistance, the low air permeability. We built these into cells. "T" means it was treated, "W" means it was washed, and "AR" means it was as received.

And that's how they failed.

The treated ones were not cycled at all, and the rest failed before they could reach a thousand cycles.

Again let me emphasize they were picked to show that we could predict failure in the separators.

(Slide 3.)

wb10

Here's another set. That ST 2140 is Pellon, 2505K4 is Pellon. Hercules is Hercules.

We put another pack in recently, 2505ML, and that's about a thousand cycles behind the rest of the cells that are running.

There have been no failures in this group.

I think one of the most important numbers to look at on this chart is the air permeability of 14, which seems to be very low, to predict that the separator might not work. But it actually does work quite well.

(Slide 4.)

These are the GAF separators, the as-received and the washed-out. It in general has properties that you think would work in a cell. There have been no failures.

As I mentioned before, every 1500 cycles we take cells out and analyze the separator again. I can't show all this data, but I have the data from 3000 cycles for the materials that are still running.

(Slide 5.)

In the first column we have the Crane pack numbers and the type of separator. In the second column we have the sample.

Now Samples 1 and 4 are towards the outside of the stack, maybe about two plates in. Samples 3 and 4 are in the center of the stack.

PACK NO SEPARATOR	SAMPLE	WET WGT / DRY WGT − 1 3000 CYCLES	THICKNESS cm × 10^3 BEFORE	THICKNESS cm × 10^3 AFTER 3000 CYCLES	ABS. g/cm³ AFTER 3000 CYCLES
22C WEX1242 W	1	0.30	22 22	21	0.15
	2	0.29			
	3	0.28			
	4	0.28			
25D HERC AR	1	1.30	21	15	0.50
	2	0.88			
	3	0.98			
	4	1.09			
31C FT2140 AR	1	0.38	24	20	0.18
	2	0.28			
	3	0.29			
	4	0.11			
38F WEX1242 AR	1	0.19	24	24	0.11
	2	0.21			
	3	0.26			
	4	0.06			
46C 2505K4 AR	1	0.84	24	16	0.57
	2	1.43			
	3	1.42			
	4	0.58			
49B 2505K4 W	1	0.83	30	20	0.42
	2	0.80			
	3	0.77			
	4	1.04			
2E 1500 CYC 2505 ML AR	1	1.59	37	17	0.62
	2	1.36			
	3	1.50			
	4	1.48			

Figure 2

SEPARATOR E1451

	WICKING cm. in .5 hr.	KOH ABSORPTION* g./cc. dry vol.	AC RESISTANCE ohm—cm.	WETTING TIME minutes	AIR PERM* cc./sec.	FAILED CYCLES
E1451 AR	6.6	0.7	34	14	1.8	320
E1451 W	0	0.7	96	>1440	1.7	997
E1451 T	0.1	0.7	32	81	1.7	25
CONTROL 2505K4 AR	1.0	–	2.8	11	61	←

*VALUES IN THIS COLUMN ARE QUESTIONABLE

RE-RUN REQUIRED

Figure 3

SEPARATORS FT2140, 2505K4, HERCULES 2505(ML)

	WICKING cm. in .5 hr.	KOH ABSORPTION g./cc. dry vol.*	AC RESISTANCE ohm—cm.	WETTING TIME minutes	AIR PERM. cc./sec.
FT2140	0	2.8	1.7	45	51
2505K4 W	0.1	3.5	2.1	57	79
CONTROL 2505K4 AR	1.0	3.1	2.8	11	61
HERCULES	3.0	3.0	1.3	...	14
2505ML AR	1.0	1.1	1.5	...	150

*VALUES IN THIS COLUMN ARE QUESTIONABLE

RE-RUN REQUIRED

Figure 4

SEPARATOR WEX 1242

	WICKING cm. in .5 hr.	KOH ABSORPTION* g./cc. dry vol.	AC RESISTANCE ohm—cm.	WETTING TIME minutes	AIR PERM. cc./sec.
WEX1242 AR	0.3	.7	3.2	14	96
WEX1242 W	0	1.4	2.9	>1440	125
CONTROL 2505K4 AR	1.0	3.1	2.8	11	61

*VALUES IN THIS COLUMN ARE QUESTIONABLE

RE-RUN REQUIRED

Figure 5

wb11

Now what we have analyzed for here is the amount of KOH, carbonate, the over-all amount of material that the separator is handling, and dimensional changes.

The third column, wet weight over dry weight minus 1, is the wet weight as it comes out of the cell compared to the dry weight after it has been titrated and washed.

As you can see, the ones we're trying to compare the polypropylenes with are the nylons. In general, that ratio comes out to be around 1, in some cases higher. The Pellons are all fairly low, except Hercules which looks like it has a similar value to nylon materials.

The next one is the thickness of the material before it went into the cycle test and after it came out. You see some of the polypropylenes don't change much, or not at all. But Hercules and Pellon change a little bit. Nylons tend to change quite a bit.

Now in the last column we have what we call the absorption of the separator, which is the grams of electrolyte or whatever is in the separator over the dry volumn. Normally nylons here come up to about .5, polypropylenes are low, except Hercules has about .5.

(Slide 6.)

I just want to show you quickly in the absorption thing what we're confronted with.

We start out with a separator that has KOH and water

wb12

in it, and we end up with a separator that has the rest of this material in it. We have all the data on the mil equivalents of carbonate, KOH, and you spot-check, anyway, on the amount of cadmium you might expect.

The first check is flooded. We really don't like that test.

The second check, on the right, is starved as it comes out of the cell.

I think what we're going to have to do is go back and make the measurement on the first piece again. We don't like the method. We have all the virgin materials that went into these cells anyway, and it's not that much of a chore to do this.

(Slide 7.)

Now let's say something about the capacity, voltages, and so forth, how the cell cycles.

Let me mention that it's rather difficult to run this many tests with different materials, and I have to give the guys at Crane a lot of credit for the way they're running this test. Pretty much you've got to play it by ear, because you've got quite a few different types of separators, and we just can't set it up like 2505ML.

However, one of the criteria I looked at on the print-outs anyway, and to cut it down to a reasonable amount

wb13

of data, was, how much does the end-of-charge voltage spread during cycling. And this data is pretty much for almost 3000 cycles.

As you can see, the four onthe top are the polypropylenes, the three on the bottom are nylons. The most interesting nylon is the 2505ML, which has a spread of 20 millivolts, which is pretty good, and it's what we like to see.

The K4 in the nylons has a spread of around 40, but it has a very high voltage. Most of these cells like to hang in around 1.50 where the ML's are down around one-four-three.

The other K4 which was washed out had about an 80 mil spread, but it's just the most random data; it just doesn't make any sense. Remember, that separator was washed out, the agent was removed.

On the polypropylenes, the only separator that hangs in there at a low value is Hercules.

The FT 2140 most of the time stays within 50 millivolts, but for several hundred cycles it went haywire; the spread was 120, and then it quieted down again.

On the extreme right we have the percent recharges that will maintain the cell capacity. We won't go to one-five-five on any cell, and we'll build up no pressure.

So it looks like in general we have to keep the recharge fairly low. The highest one being Hercules, and the

wb14

lowest being standard nylon.

There's another interesting thing that came out of all this. We all know that the voltage of the ni-cad decays with cycling. And call it what you want, but we start out with a nice flat curve and eventually it works its way down a little ways.

I'm not picking any separator here; they're all about the same as far as this curve goes.

(Slide 8.)

For instance, this is the 2505K4 as received. On the first acceptance test that we did at Crane, there are the ampere hours out to the various voltages. In other words, where the arrow is sitting on top of it, that's the average of the six cells to 1.2 volts. The next line over is the average to 1.15. The next one is average to 1.0, and the next one is 0.5.

And then we give it another capacity check. And, for some reason, most of these cells kind of lost on this second capacity check. But they were all well over 7, so we didn't worry about it too much.

But now after we cycled it for 1500 times, this is the capacity here, for 1.15. That used to be the capacity, 1.15; okay? So it's just over - slightly less than 4. And I didn't bother with the rest. We just plotted-- Oh, yes: this is to 1 volt and this is to half a volt.

wb15

So, when you look at it, we're not doing too bad in holding capacity to half a volt, or even a volt.

There is our decay, which most people don't like to work with; the Systems guys, anyway; because it's a little difficult.

Of course, then right after we do that 1500 cycles we do another capacity check. And all the cells built back up again.

(Slide 9.)

There's the capacity, 1.2, 1.55, 1, and 0.5.

An interesting part about this, no matter what separator we use, all seven we're running right now, they all show the same characteristic. Some are a little worse than others. I didn't really have time to show them all. I just wanted to show the general trend.

I think that's about it.

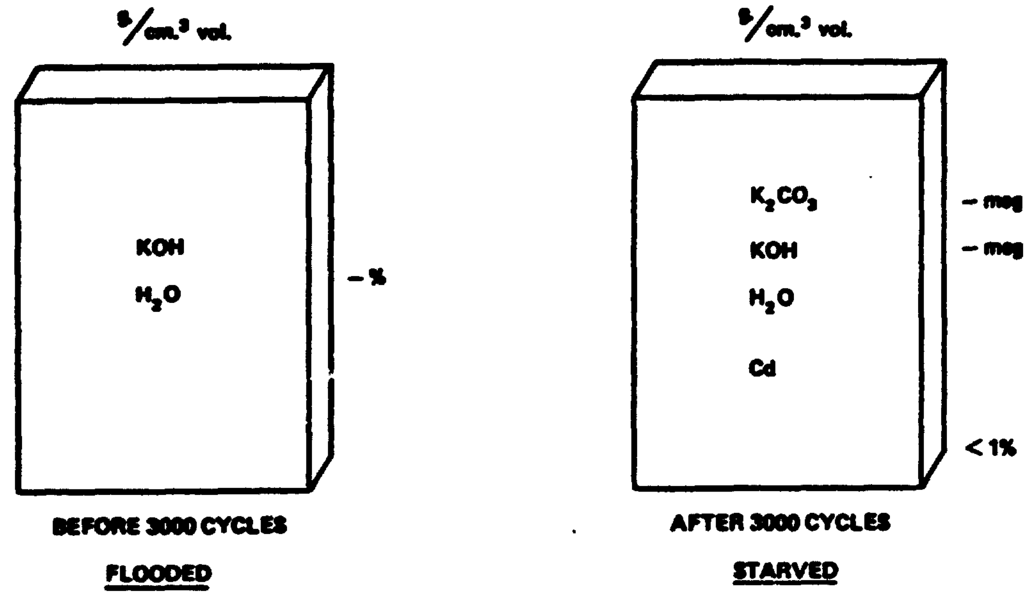
Here's how they recover. It might be of interest to you.

(Slide 10-11.)

This is a print-out of the ampere hours versus the voltages. For instance, let's-- On cycle 1422; I normally refer to this as 1500 cycles; here's our capacity, to 1.15, here's our capacity to 1, and here's the capacity to .5.

It's really not capacity here; it's plotted in time. In other words, 2 is 6 ampere hours.

Here's the recovery on cycle 1423. Here's the capacity to 1.15, to 1, and to .5.



KNOWN – LENGTH, WIDTH, THICKNESS
WET WEIGHT & DRY WEIGHT
POSITION IN CELL

Figure 6

PACK NO SEPARATOR	VOLTAGE SPREAD EOC MV	% R.C.
22 C WEX 1242 W	70	105
25D HERC	30	110
1C FT 2140 AR	50 (120)	101
38F WEX 1242 AR	90	105
46C 2505 K4 AR	40 (1.50)	105
49B 2505 K4 W	80	103
2E 2505 ML	20	103
TEMP 20°C		

Figure 7

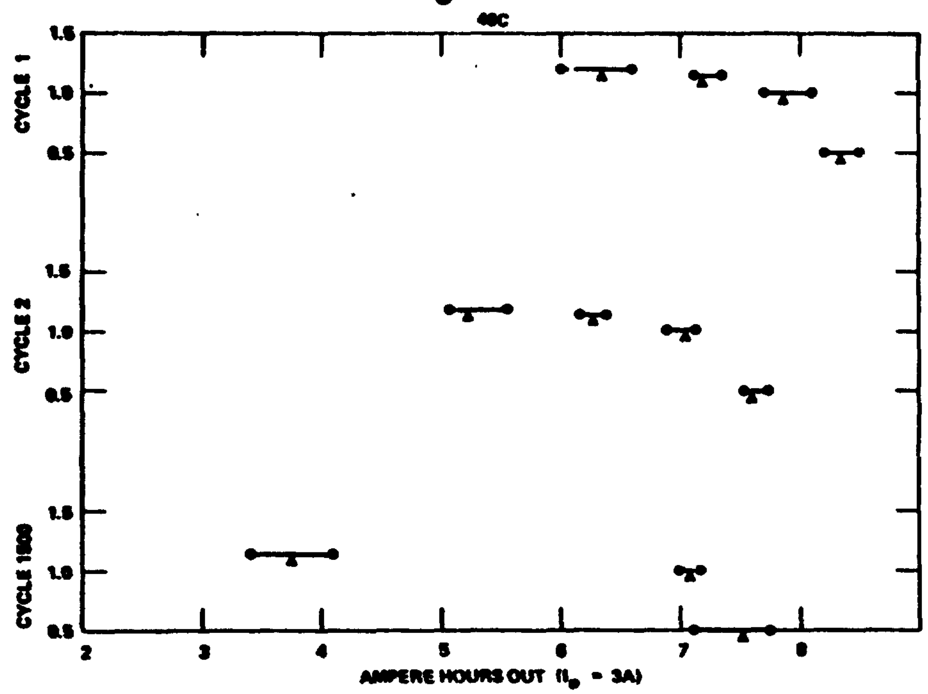


Figure 8

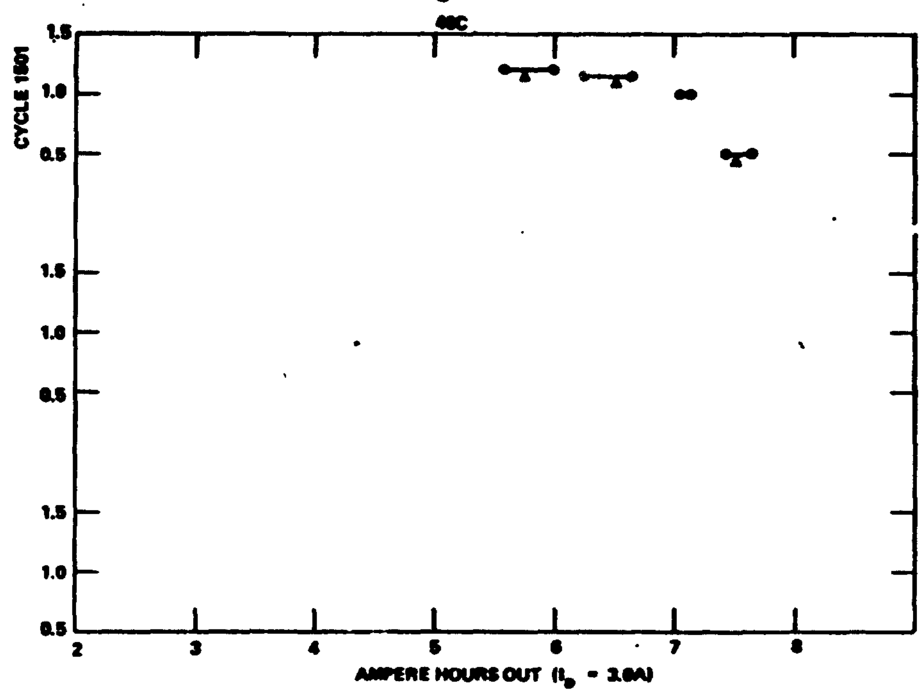


Figure 9

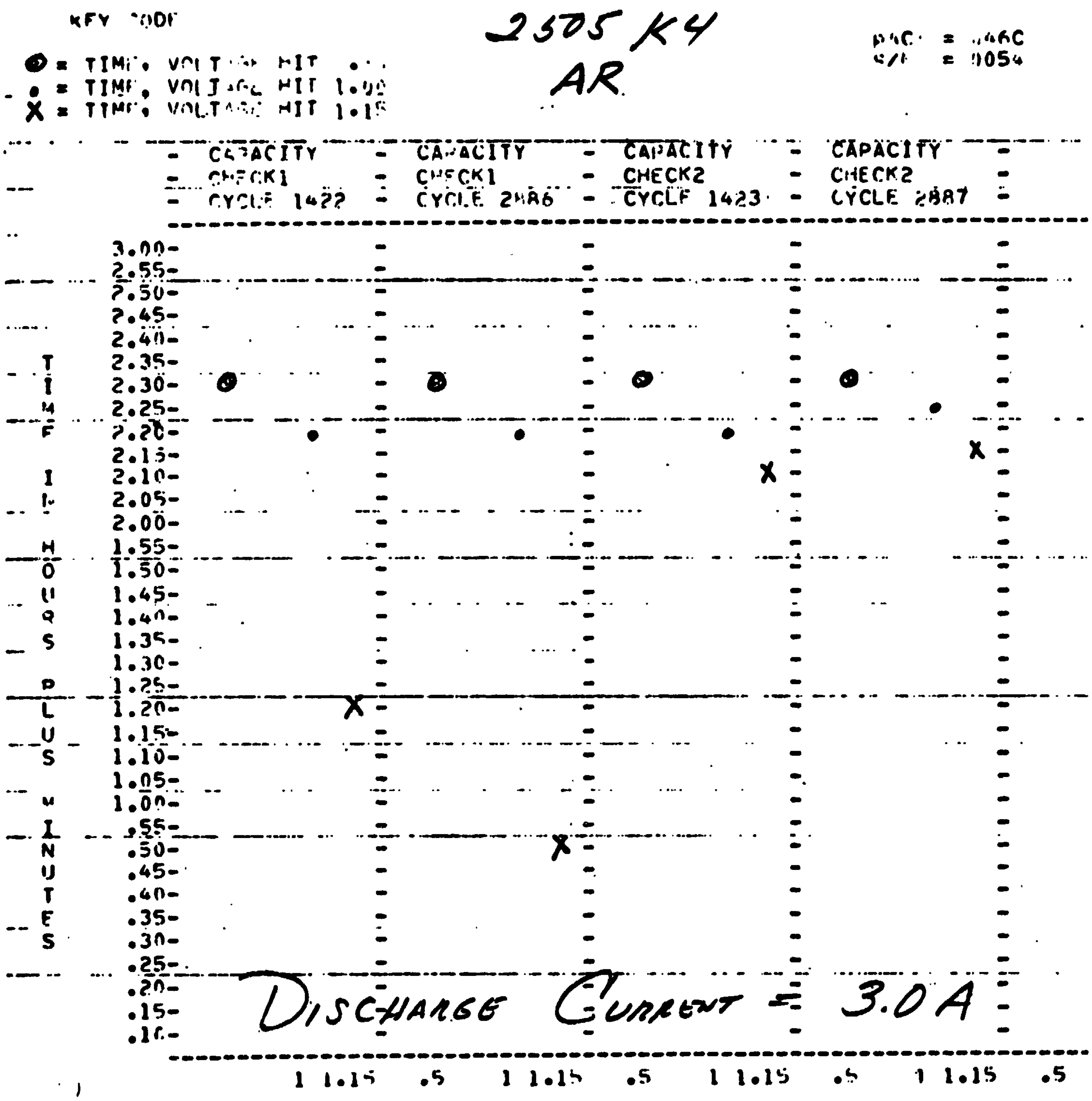

KEY CODE
TIME, VOLTAGE HIT 1.02
X = TIME, VOLTAGE HIT 1.15
2505 K4
AR
S/N = 0054
CAPACITY CHECK1 CYCLE 1422
CAPACITY CHECK1 CYCLE 2886
CAPACITY CHECK2 CYCLE 1423
CAPACITY CHECK2 CYCLE 2887
TIME IN HOURS PLUS MINUTES
3.00
2.55
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
1.15
1.10
1.05
1.00
.55
.50
.45
.40
.35
.30
.25
.20
.15
.10
DISCHARGE CURRENT = 3.0A
1 1.15 .5 1 1.15 .5 1 1.15 .5 1 1.15 .5

Figure 10-11

wb16

Here's our capacity check at cycle 3000, approximately. We go down again, then it recovers again.

In general, all cells do this. But there are a couple now that are getting weak. One or two of the polypropylenes seem to be weak.

We get this data on every cell. So it's not the pack getting weak, it's cells here and there getting weak.

Well, that's about it. It's an awful lot of data that I went over rather quickly, I guess.

So, do you have any questions?

Mr. Font?

FONT: Font, SAFT. Did you adjust the amount of electrolyte in your different --

HENNIGAN: Yes, I had to.

In general, for most of the cells that are running right now it's about 4 cc's per ampere hour, 4.3 cc's per ampere hour.

I think the Hercules and the Pellon have the same amount. The others may be a little bit less, maybe a cc or so.

Fred Betz?

BETZ: Fred Betz, Fairchild. Two questions, Tom.

One, do you have any explanation for the performance of the Hercules with the low permeability? In other words, air permeability has generally been accepted as being a reasonably critical factor. And Hercules was fairly low.

wb17

That's the first question.

Second, is there any explanation for the high recharge required on Hercules? Are they related?

HENNIGAN: I don't have any explanation for that low air perm. And the separator works right, as I mentioned. If I had looked at the separator before, it might be one I might not have chosen.

The reason it was chosen, though, is because it wets so well, wicks. For instance, the number we had to do wicked 30 centimeters in half an hour; for the rest, some don't even wick at all.

Why do we need the 110 percent? The rule we are working with out there is to make sure we get enough capacity back in the cell so it won't run down on us. And you keep the voltages down, and so forth. But to push them as hard as you can. In other words, if those cells would take 120 percent we would charge them at 120. But they won't do it. So we try to push the cells as much as we can.

I don't know how it would work at 105.

Are there any other questions?

Will Scott?

SCOTT: Scott, TRW. On one chart you showed a list of end-of-charge voltage spreads, and than in another column was recharge percentage. Were those data connected on any one line? --that is, did the voltage spread shown

wb18

correspond to the recharge ratios shown; or was that independent data?

HENNIGAN: The spread is gotten by eye-balling the computer print-outs. They change a little bit. So you kind of eye-ball them, and you get the spread for about 3000 cycles.

The percent recharge that I had there is data I have been getting on about every thirtieth cycle. And after the first couple of hundred cycles that's about where we set them at.

So for a specific cycle I can get you that information; but it wasn't on our chart.

SCOTT: Are you saying, then, that the voltage spreads that you showed did not necessarily correspond to the recharge percentage that you showed on the same line?

HENNIGAN: Right.

It's a good point. Maybe I ought to look at it a little closer. We have quite a bit of data on these tests, right now, and it's a little hard to absorb it all.

LACKNER: Lackner, Canada Defense Research.

Further on this percent recharge, I'm not too sure just what's meant. By the 110, 105, 120 percent recharge, is this all that it would tolerate, all that you program for before you get a high end-of-charge voltage? Or could you continue the overcharge for several thousand percent?

HENNIGAN: We tried to do 120 percent on all cells to kind of accelerate it somewhat. We couldn't do it. The voltages were going too high. And in some instances we were getting pressure build-up. That particularly happened to the E1451 material.

So we had to cut back in the power supply until they would stay below one-five-five and we had no pressure.

LACKNER: This is what I thought you meant. Because the question had come up on air permeability, and by and large the better the air permeability -- and we've been working in the area of something like 120 cfm to 200 cfm -- you can overcharge -- the better the air permeability the better the chance you have for the oxygen from the positive to recombine with the negative. And you're not going to get pressures built up. And we find that you could charge the cells at C/10 for 120 hours and more and keep your voltages below one-five-five and your pressures below 75 psi without any problems.

So air permeability is the criteria that you have to aim for.

HENNIGAN: Art?

WROTNOWSKY: Art Wrotnowsky, GAF.

Tom, would you repeat your comment on wetting, the wetting time? Are you referring to wicking, or time to wet? You said that it took thirty seconds to wet out the Hercules

wb20

separator?

How does that go, again, please?

HENNIGAN: It wicked 30 centimeters in half an hour.

WROTNOWSKY: Vertical wicking?

HENNIGAN: Right.

WROTNOWSKY: Thank you.

HENNIGAN: There was another question there. Bob Shair?

SHAIR: Bob Shair, Motorola.

Did you see any correlation between either end-of-charge pressures or steady state overcharge pressures with these various separators?

HENNIGAN: After we do the capacity checks, of course in the beginning, too, we do overcharging. And when we do these tests the pressures are not better or worse; they're about the same order of magnitude as we get during cycling.

Most of these cells, the pressures are of the order of 20 to 30 pounds gauge.

Well, if there are no other questions, Will Scott would you give your talk on some of the separator work being done by TRW?

SCOTT: My comments are going to be in two areas regarding separators. One is in the area of the present state of the art of separator testing and test methods, and the other is a little bit of data on cell testing with

wb21

polypropylene separators versus nylon separators at deep depths of discharge.

We have not done -- not gotten a lot of data such as of the type that Tom just showed you, but we do have a little of interest under some special test conditions.

I guess first I would like to make some general comments on separator testing as is being done today.

I recently made a list of the various different kinds of separator tests that are being done today. Most of them have been published in one form or another in connection with several activities going on, one being the work on separators done at Tyco for Goddard a year or so ago, another being some of the methods that appeared in the NASA Interim Specification, a third being some test methods that were published by Eagle-Picher in connection with their work on process variables.

With a certain amount of interpretation I listed fifteen different test methods, not all of which are independent. And what I tried to do is categorize these into two types, not necessarily exclusively, but to try to decide whether the test was of use for quality control and/or whether it was of use for evaluation in terms of actual cell manufacture and cell performance.

I would like to show you that list.

(Slide 12.)

SEPARATOR MEASUREMENT CATEGORIES

	USEFUL FOR:	
	QUALITY CONTROL	SEPARATOR EVALUATION
THICKNESS	x	?
WT./UNIT AREA	x	?
TEAR STRENGTH	x	?
BURST STRENGTH	x	?
AIR PERMEABILITY	x	x
ELECTROLYTE ABSORPTION	x	?
WICKING RATE	?	?
WETTING RATE	x	?
WET STRENGTH	x	?
FOAMING	?	?
EXTRACTABLES	x	?
INORGANIC CONTENT	x	?
OXIDATION RESISTANCE	?	x

? = correlation with cell performance not established to date.

Figure 12

wb22

I'm not going to read all these off, but you can see that they fall into the area of inherent physical characteristics of the separator, and various chemical and physical characteristics obtained by operating on a separator by solvents, electrolyte, and so forth.

On the first column I checked off all of those that appeared to me to be primarily or largely -- not necessarily primarily, but useful for control, quality control in terms of separator manufacture and cell manufacturing.

In the second column I tried to indicate, at least to me, which I felt sufficient information was available today to say that these particular tests made a definite contribution to cell performance, and where I could not come up with any information at all that I was aware of that would convince me of the direct correlation between a particular cell separator characteristic or test and cell performance, I drew a blank. For those with a possibility but certainly not established at this point in time, I put a question mark.

So this is what I got.

It's apparent that most of these test methods that I've listed here appear to be of the type that could be used for quality control. But there is a lot of information missing on the correlation between these separator characteristics and the performance in the cell.

I think that certain comments that have already been

wb23

presented here this morning tend to bear this out; that is, there is a lot of testing and data being gathered that we know right now the characteristics do not appear to correlate with cell performance. There actually appear to be some negative correlations, and so forth.

So I would like to see, myself, some more thought and work done in the area of developing test methods and characteristics of separator materials that we know correlate with cell performance.

The test data that I mentioned is under the following conditions: The test data was in connection with a program that was directed toward operation of batteries in synchronous equatorial orbits, where we have relatively few total number of cycles required for lifetime, but a requirement for maximizing the utilization of the energy from the battery.

So we are pushing depth of discharge.

The conditions of the test were: cells were operating at an average temperature of approximately 40°F. We are operating at this temperature for various reasons, most of them connected with trying to optimize the life of the battery, because we are interested in a minimum of seven years of operation in orbit for this particular application.

The test conditions are a 12-hour cycle consisting of approximately eleven hours of charge period and one hour of

wb24

discharge period. The cells are being operated to approximately 90 percent of their nominal capacity on every cycle. This is a form of accelerated test that we are using.

The cells that we have on test are few in number, there is a total of six right now that we have any significant amount of cycle data on. There are three 20-ampere-hour cells with two different kind of polypropylene separator material.

By the way, we have tested under similar conditions cells with Pellon 2505 separator in them, in the past, and I don't have the detail of the data with me, but what we are basically doing, of course, is trying to compare the performance of the cells with polypropylene with those with the nylon as a reference.

Our data consists of only the performance from the cells with one type of polypropylene, namely GAF WEX 1242, and one other kind, which is Pellon FT 2140.

Now what we have done is to perform thirty of these cycles in a row, and then put the cells on continuous low level charge for a period of approximately one week. And then we have done another thirty of these cycles, and then another period of continuous low level charge. And to date we have completed five of these thirty-cycle sequences.

What we have seen is a performance with all six of these cells under these conditions that I consider to be superior to the performance with the nylon Pellon 2505 separator

wb25

material.

We were concerned initially with two possible problems with the use of polypropylene under these conditions. At this lower temperature there is a possibility of some pressure problems if the polypropylene would possibly impede oxygen recombination because of the normally lower oxygen recombination capability of the negative electrode at these lower temperatures. So we were concerned that this effect might be accelerated due to the possible characteristics of the polypropylene materials.

The other general problem that we were concerned about was the possibility of adverse effect of electrolyte migration under these conditions, where the electrolyte might, as a result of cycling and accumulation of life, migrate away from the separator permanently into the plates and give a high resistance separator condition.

Well, to date at least with 150 cycles to 90 percent depth of discharge under these conditions we have seen no external evidence of any problems. The pressures at the end of charge are within the same range, within the normal spread that you see in most cells, that we have seen with nylon separators.

Under these particular conditions, at lower temperature, you usually have to tolerate higher pressures that you do at room temperature. And we consider pressures up to

wb26

50 psig as quite normal under these operating conditions.

By the way, the recharge ratio that we are using is 110 percent. We have had no problems at all from pressure or voltage on these test cells under that set of conditions.

The end of discharge voltage is in general slightly higher on these cells than it was on comparable cells that we tested about six months ago that had nylon separators. But I don't believe the difference is-- The difference is still within the normal variation from cell to cell.

That's what I have to say.

O'ROURKE: Dr. Scott. Joe O'Rourke, Grumman.

On the chart that you had up on the screen, where you had the various separator properties and you had which particular properties you felt were highly correlated with cell performance, what was your criteria for cell performance, and what type of analysis was used to come up with the correlation?

SCOTT: Well I must admit that that chart is relatively subjective at this point in time. However it is the result of looking at the kind of data that Tom Hennigan has in his pocket, and others that I have been able to run across, mostly noting, I guess, the occurrence of negative correlations; that is, where, for example, one might obtain, say, a very low electrolyte pick-up in a particular sample of separator, then build a cell with it, and get

wb27

exemplary performance from an electrical standpoint and cycling standpoint from that cell. That I consider to be the type of thing where I would tend to draw a blank, or, obviously, at least a question mark as far as lack of evidence is concerned.

But, as I say, I haven't done a lot of quantitative analysis, really. This is just an impression that I have right now from the tests that are being done.

O'ROURKE: The reason I brought this up, it wasn't the type of analysis that Eagle-Picher is doing in a process variable study, in other words, a regression analysis; this was not a formal regression done against a particular dependent variable using those various separator properties? It was nothing as formal as that?

SCOTT: That's correct.

I do feel that not enough of that kind of analysis has been done. And, as a result, I would just caution anybody to give a little bit of thought to whether or not they might be spinning their wheels making a lot of separator tests without really knowing whether there is going to be any correlation or not.

HENNIGAN: Are there any other questions?

(No response)

As far as separator tests, what you might call characterization tests, we've never been happy with them at all. And presently we have a contract with the Bureau of

wb28

Standards, and Mr. Aaron Fisher of Goddard is the technical monitor. We have all these virgin materials that we ran in these tests at Crane. And, Aaron, could you say a few words on the type of tests that the Bureau of Standards is going to do?

FISHER: What I wanted to say is that NBS is still in the process of looking at the particular tests and examining them and seeing which appear as thought they might be interesting or fruitful.

Essentially the tests are the types that were indicated in the Fleischer handbook, the Air Force Handbook. ??

Aside from that, I would like to indicate a couple of things that we found during our particular studies on materials and throw some more light on the facets of what the materials are. This would be a continuation of the information that Tom has shown.

The ideas concern themselves primarily with some of the SEM types of photos. From these SEM photos you are able to see the differences in structure or in rod length or diameter or any particular flattening that may have occurred during processing. These observations lend credence to Tom's indication that he picked a certain type of material because he thought it was going to be a poor material. And maybe some of these photos and other indications I have may show why it would be material like that, a poor one.

(Slide 13 - 16.)

This is the Hercules material that Tom was talking about. And we have magnifications here that run from 1000 over in this area, 2500, and then 250, et cetera. It may be a little difficult to ascertain the differences between this and the subsequent one, but I will try to put an overlay of one on top of the other so you can make some sort of contrast between how much smaller in diameter one particular type material is than the other.

I have samples of the 1451 that I would like to show you over here.

(Slide 17 - 19.)

You can see the difference in the 1000. Now this is a 1000 magnification here, and this is the 1000 magnification right up over here. And the difference is more than a factor of 10. So that we have one particular fiber which is very slender and one particular fiber which is quite thick.

The other thing which is apparent on the Kendall material was that it was a highly densified type material, as you can see over here by the flattened aspect of the filament.

Now in subsequent work that the Bureau of Standards has done, it was indicated that the density of the material has risen to about .60 -- that is, the density of the film structure, of the non-woven film structure, had risen to about .60. The maximum density it might have achieved was something

SEM PHOTOS HERCULES POLYPROPYLENE SEPARATOR RT-37-2665-15
50X - 2500X

50X

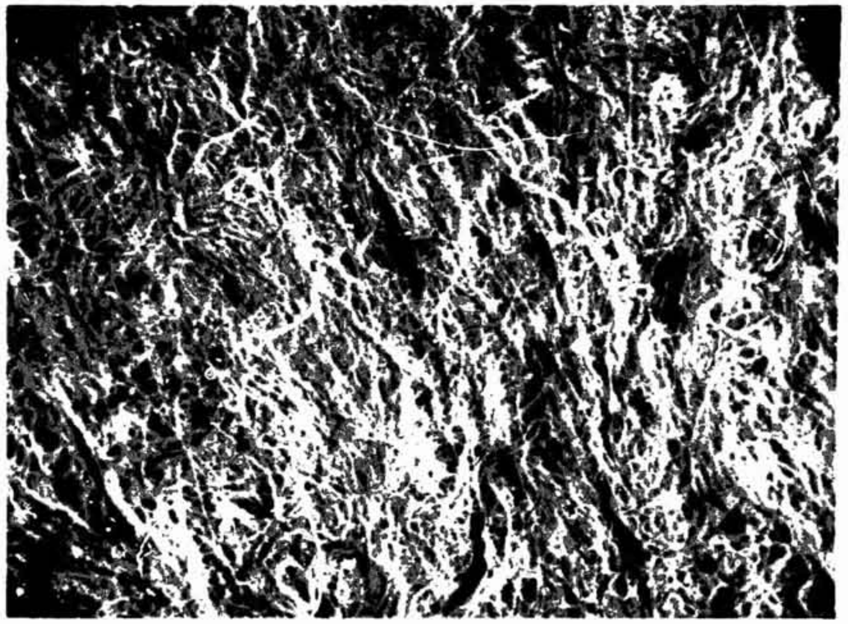


Figure 13

250X

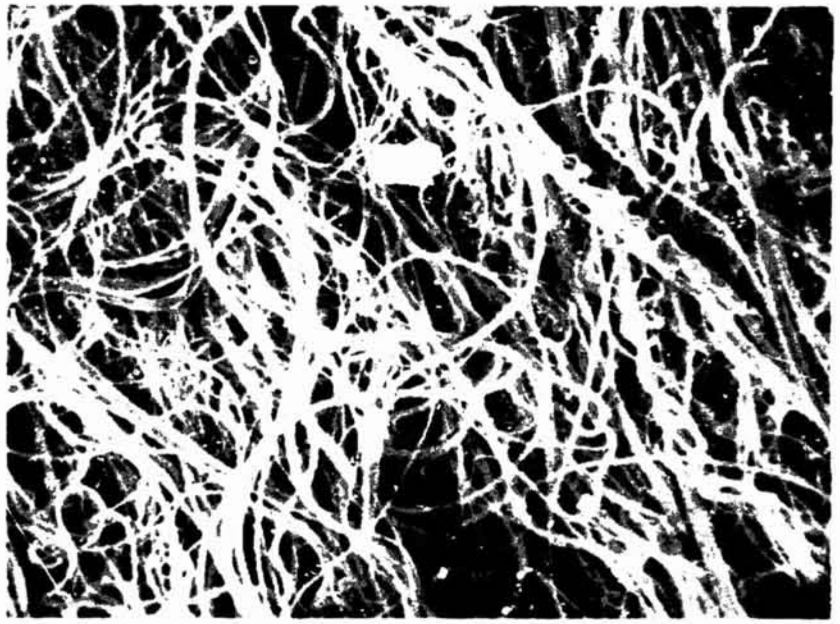


Figure 14

2500X

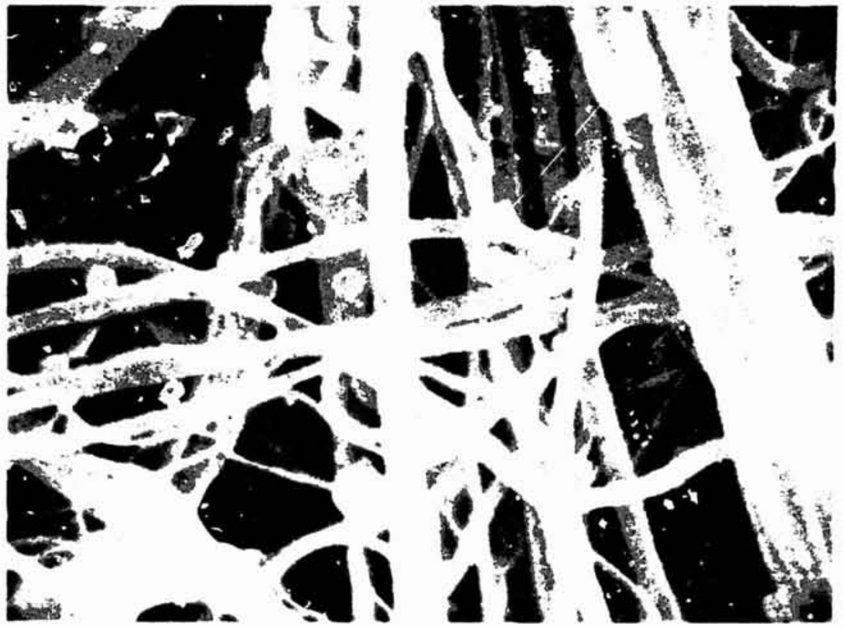


Figure 15

1000X

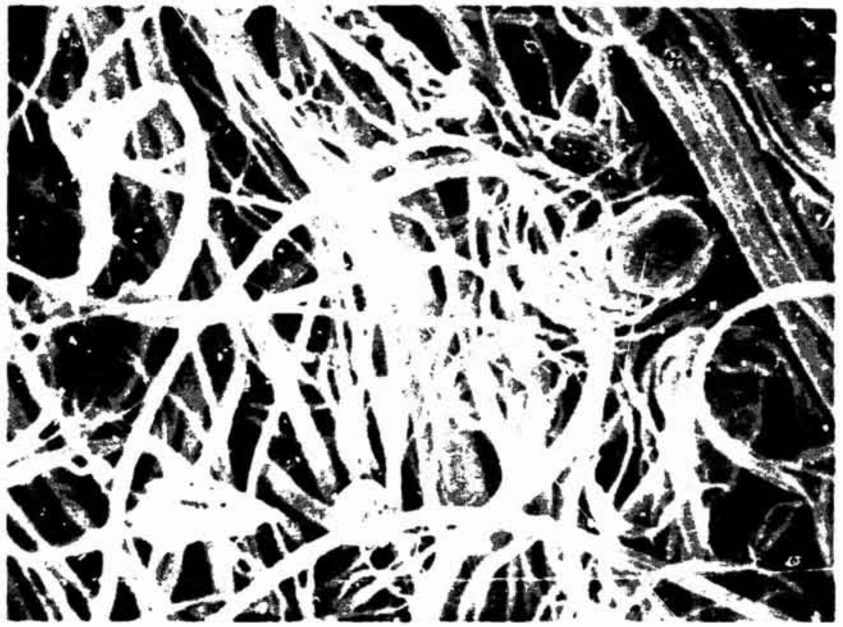


Figure 16

SEM PHOTOS KENDALL POLYPROPYLENE SEPARATOR E - 1451

50 X - 1000 X

50 X

Figure 17

250 X

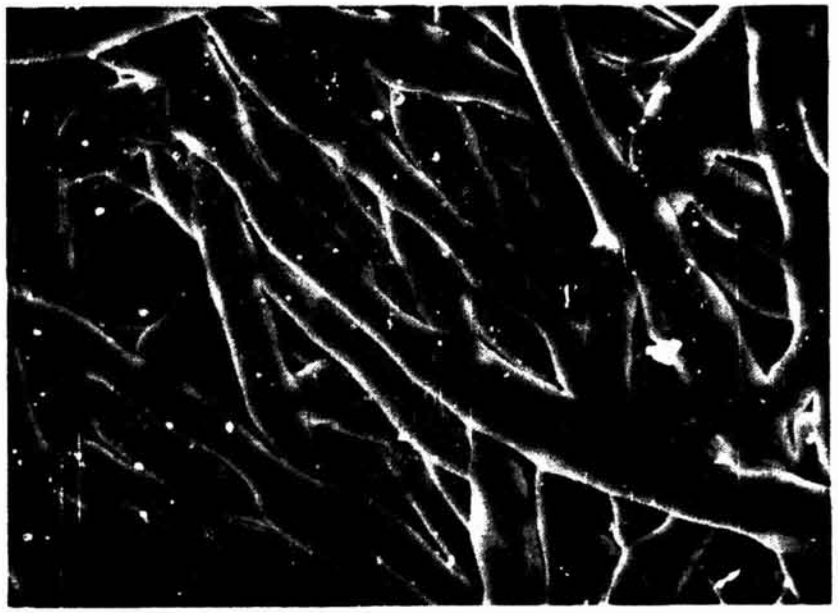


Figure 18

1000 X

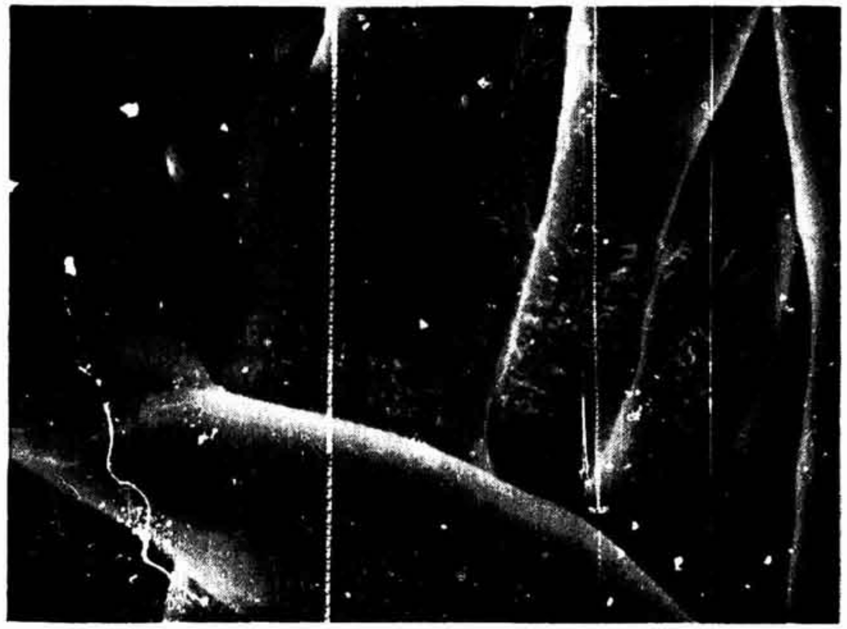


Figure 19

like about .90, whereas the apparent density for the Hercules material was in the neighborhood of about .20.

We have here some additional information which indicates the differences between the two types of materials,

(Slide 22.)

that is actual tensile strengths that were taken of the materials. And it indicates that the E1451 is very high, as compared to the others in both the transverse and the machine direction in regard to ultimate tensile.

So just looking at ultimate tensiles, now, we have an indication that one material is going to have a higher density than the other material, and possibly a lesser porosity; and, because of that, the permeability to the oxygen might be decreased. Therefore, just looking at the tensile data gives you a feel for the suitability of a particular type material.

Now we're also looking -- I have here a little chart on the fiber diameters that were actually measured from the pictures.

(Slide 23.)

It shows the E1451 averages about .001, "whereas the Hercules material is .00005." I said a factor of 10 before? It looks more like a factor of about 20.

Now, that may indicate one of the reasons why the wicking is so great with the Hercules material, in that with

COMPARATIVE ULTIMATE TENSILE STRENGTHS OF TEST SEPARATORS IN PSI

	As Received		After 48 Hour Soxhle & Hot Water Wash	
	Transverse Dir - Wet	Machine Dir Wet	Transverse Dir - Wet	Machine Dir Wet
Pellon 2505 ML - as rec'd	177	317	398	321
Pellon 2505 K4 - as rec'd	585	790	781	751
Pellon 2505 K4 - Acid treated	711	511	552	164
Kendall - E 1451 - as rec'd	558	2927	635	2940
Kendall - E 1451 meth wash	1611	7977	1682	7208
Kendall - E 1451 - meth & acid wash	1141	5720	1298	6089
Pellon 2140 FT - as rec'd	1092	383	1200	395
GAF WEX 1242 304PO - as rec'd	817	856	786	644
GAF WEX 1242 304PO - meth wash	871	885	931	917
Hercules RT-37-2665-15 as rec'd	11	68	15	26

Figure 20

APPROXIMATE SEPARATOR FIBER DIAMETERS TAKEN

FROM

SCANNING ELECTRON MICROSCOPE PHOTOS

	Material	Diam
Kendall	E 1451	0.0010
GAF	WEX 1242-304PO	0.0005
Pellon	2505 ML	0.0005
Pellon	2140 FT	0.0007
Hercules	RT-37-2665-15	0.00005

Figure 21

AVERAGE MOLECULAR WEIGHTS

GEL PERMEATION CHROMATOGRAPHY TECHNIQUE*

	Material	Aver. Molecular Weight
Kendall	E 1451	224,700
GAF	WEX 1242-304PO	235,500
Pellon	2505 ML	2130 Å**
Pellon	2140 FT	48,400
Hercules	RT-37-2665-15	14,100

* Waters Assoc.
** Effective size in solution

Figure 22

COMPARISON OF KENDALL E-1451, EARLY CRANE CYCLING FAILURE (UNDER 1000 CYCLES)

AND

HERCULES RT-37-2665-15 (STILL OPERATIONAL AFTER 4000 CYCLES)

Material	Property	
E-1451	Apparent density gms/cc	0.60*
	KOH absorbtivity gm/cc (aver. 3 types)	0.26
	Porosity % (aver. 3 types)	20.6
	Resistance ohm-cm (aver. 3 types)	151.0
RT-37-2665-15	Apparent density gms/cc	0.20
	KOH absorbtivity gm/cc	0.91
	Porosity %	70.0
	Resistance ohm-cm	11.6

*Maximum density possible 0.90 for solid polypropylene

Figure 23

a wetting agent on, and so much surface area, the KOH might really be inclined to move quite rapidly.

One other area that we have looked at in order to see whether there might be a possibility of ascertaining degradation from a before-and-after type of arrangement, is, that we had the Waters people do average molecular weights for us via gel permeation studies. And we have come up with indications of molecular weight, which we might see later as being changed, as a function of the battery operation. I might indicate some of the values that exist over here.

(Slide 20.)

We have the Hercules with a comparatively low average molecular weight, about 14,000, and the E1451 and the 304PO having the highest molecular weights.

Now it will be interesting, on removing some of these separator materials at a later date, after failure, to see whether these molecular weights have, in effect, changed, whether there has been any kind of breakdown in the structure of the material.

(Slide 21.)

Some of the preliminary information that we have gotten from NBS, I've taken some of that material -- and it may or may not be valid at the present time, but I've tried to make a comparison of both the Hercules material and the material which failed. And as noted before, the density of

wb32

the E1451, which is Kendall-- Incidentally, we're not deprecating this Kendall material; I'm very happy that it was put in here, because it's a real basis of comparison which may lead us to make some kind of conclusions.

The Kendall material density runs about .60, and the Hercules material is about .20. The absorptivity of KOH has been .26 versus .90 for the Hercules. On a porosity basis we have about 21 percent for the Kendall versus about 70 percent for the Hercules material.

And in the ohms area, we have ohm-centimeters about 150 versus 11.6 for the Hercules material.

Now as I indicated before, these are in the process of being delineated. But both materials received the same type of test in this particular work that is being done at NBS.

I have just presented these things for what they're worth, and the fact that they may be able to help delineate, or set forth some of the properties that might be required in a separator material. I guess everything will have to depend on the longevity of the particular tests that Tom is running over at Crane.

That's about all.

HENNIGAN: Do we have any questions for Mr. Fisher? Mr. Dangel of Kendall.

DANGEL: I'm from Kendall. We've been doing some

33 more work recently, particularly on this density problem. And we have several new materials, and they bear particularly on this density thing.

If you'd like, I'd project them.

FISHER: Yes.

DANGEL: Okay.

(Slide 24.)

Aaron mentioned that density readings from .60 up to .90 were obtained, depending on the amount of compression that was done.

This new category has readings between .20 and .30, and also we have vastly increased the air permeability from minimums of about 80 against readings of -- what? -- 20, was it? -- and actually up into the 300 range. And some of this has been achieved purely by improvements in how we process the stuff, and some of it by manipulation of fiber diameters; that is, using fibers of different diameters and combinations thereof.

These materials have been in the laboratory for over a year now, but we're about ready to release them to anybody who would like to do some test work on them.

Thank you.

HENNIGAN: Are there any further questions?

I might add that we intend to build some more cells, and we would be interested in what materials that you have.

TENTATIVE SPECIFICATIONS

Polypropylene Low Density WEBRIL Nonwoven Fabrics

Style No.	Weight (g/sq.yd)	Thickness (CADY)	Density (g/cu.cm)	Frazier Air Permeability cu.ft./sq.ft/min. @ 1/2" H_2O	Tensile Strength lbs/in. Minimum M.D.	C.D.
XM 1247	42	.0095	.21	325	15	1
XM 1249	50	.008	.29	80 min.	15	1
XM 1250	50	.008	.29	80 min.	15	1
XM 1253	60	.0096	.28	80 min.	10	0.5

Figure 24

wb34

We'll have to get back to the separator thing after the break. We're running pretty late. We're supposed to get finished with the seals this morning, but that doesn't look like it's going to happen. But we'll do what we can.

Let's take fifteen minutes' recess, and try to get back at eleven.

(Recess)

wbl

HENNIGAN: Will everyone please take his seat so we can go on with the meeting?

As I mentioned before the break, we're running kind of late, and we hope to get through with the separators and seals this morning but it doesn't look like we're going to be able to.

We have one more bit of information on separators from the Bell Telephone Laboratory, from Dean Maurer.

MAURER: We have some applications in the Bell System for sealed nickel-cadmium batteries to support semiconductor memories to prevent their volatility.

These batteries are subjected to rather high temperature ambient for extended periods. They're on continuous overcharge.

This is a somewhat different kind of use mode than what you've been talking about here this morning, but I think some of the same problems can show up.

We knew that cells with nylon separators would not perform well under these conditions; the nylon would degrade and possibly cause shorts, or result in a charge negative from the oxidation of nylon.

So we obtained some cells with polypropylene separators to determine what kind of failure modes and life characteristics a cell with that kind of separator would have under these conditions, and see what the next failure problem

wb2

might be in this system.

These cells were of the cylindrical type. The size I can describe as being one-third C. They had capacity around 400 milliampere hours. They had polypropylene separators, as I said. And all of the other material within the cells were non-degradable, except for an insulating grommet at the top of the core, which also formed part of the seal area. And that remained as nylon.

We put these cells on test, and, as I say, our use mode was continuous overcharge. So we looked at several different temperatures and several different overcharge currents, and the results were consistent from one temperature and current to another.

(Slide 25.)

These are typical. This is the voltage as a function of time on overcharge at temperature. The temperatures ranged from 110°F. to 180°F, and the overcharge ranged from roughly C/40 to roughly C/10.

These are six cells under these conditions. There were six for each condition. And we plot here the voltage. And you can see there's a reasonably flat area followed by a very sudden rise in voltage. This marked the venting of the cell. The negative had become fully charged and generated hydrogen, and the cell vented.

Similar results were obtained at all temperatures and all currents. And there was some discussion earlier about the end-of-charge voltages and their spread. These might be considered typical for what we obtained on all of these cells.

They were relatively stable ov r the test period until this failure event occurred.

We analyzed these data statistically, making a probability plot, log probability, of days to failure versus percentage normalized by this function for small samples, --

(Slide 26.)

-- and, again, a reasonably good fit to normal, log normal, distribution for these cells.

(Slide 27.)

Then plotting all of this data on days to 50 percent failure -- in other words, the mid-point on those previous curves -- versus one-over-T, we got results that look like this. There are three different overcharge currents shown here and the four different temperatures. They are reasonably good straight lines within a given current.

So if we want to determine the failure mode now of these cells, the failure mechanism, rather, we need to explain the temperature dependence, and we need to explain the dependence on the charge current.

(Slide 28.)

The nylon grommet in the cell was, again, across the

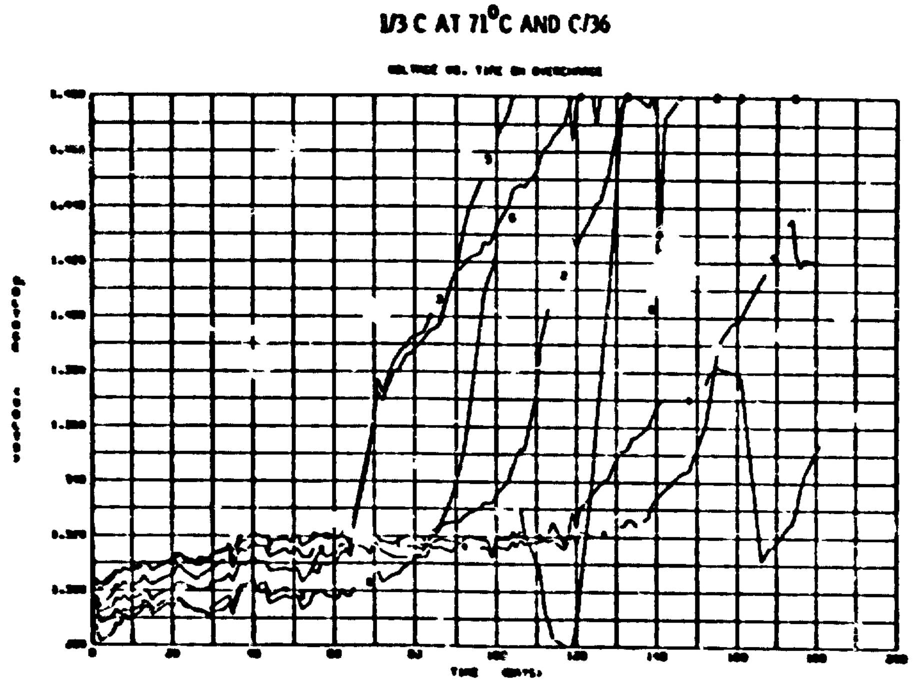


Figure 25

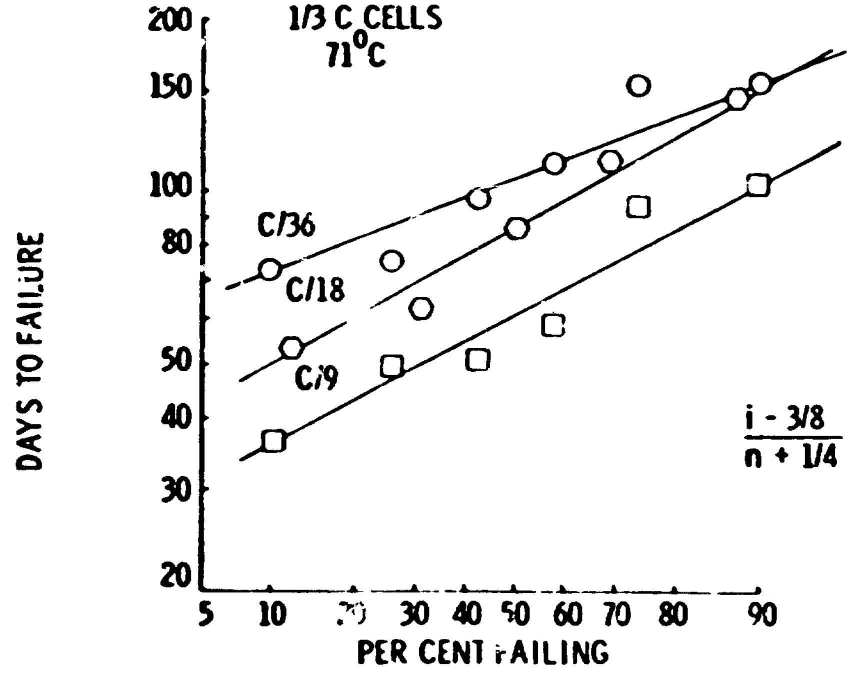


Figure 26

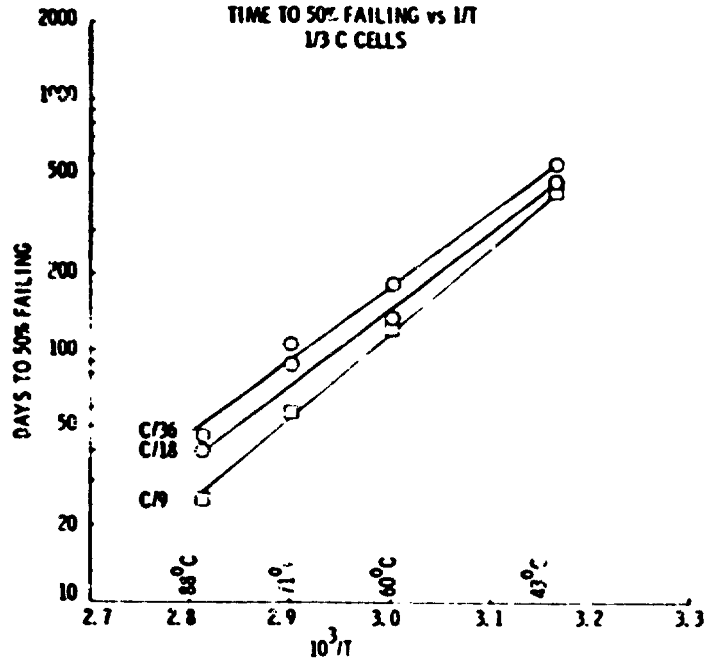


Figure 27

PROPOSED MECHANISMS

1. NYLON REACTS WITH NEGATIVE.
2. DIRECT OXIDATION OF NYLON ON POSITIVE.
3. DIRECT OXIDATION OF NYLON BY OXYGEN.
4. OXIDATION OF NYLON DECOMPOSITION PRODUCTS BY OXYGEN.
5. ELECTROCHEMICAL OXIDATION OF NYLON DECOMPOSITION PRODUCTS.

Figure 28

wb4

top of the core. There are several mechanisms one can propose here. One is that the nylon reacts with the negative and charges it by some mysterious means; which can be ruled out, because the nylon is not in contact with the negative. Nor is it in contact with the positive, so a direct reaction there is not possible.

There could be a direct oxidation of nylon by oxygen in the cell, some oxygen pressure dependence which was related to the charging current. Again, this can be ruled out by the stability of oxygen in air.

We could have oxidation of the nylon decomposition products, nylon hydrolizing, decomposing in the electrolyte, and these products then reacting with oxygen. This mechanism is plausible in that presumably there could be a rate dependent step of oxygen on these products.

We made some bomb experiments in which we exposed these nylon grommets to an environment of potassium hydroxide and 100-pound pressure of oxygen, and followed the oxygen pressure decay as a function of time at temperature. This did occur, and it had an activation energy in the vicinity of 30 kilocalories per mol.

Unfortunately, the activation energy that was obtained for the cell decomposition from these data is between 14 and 15 kilocalories per mol. So the mechanism is viable,

C.2

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but it doesn't fit the data.

The last mechan... n: an electrochemical oxidation of these decomposition products. John Broadhead in our laboratory found that nylon decomposition products showed an oxidation step in potential scan studies. So that these products could be electrochemically oxidized on the positive electrode.

(Slide 29.)

So we can then work up an over-all mechanism to explain these results now.

The time to failure, $T_{1/2}$, will be equal to the quantity of negative, excess negative that has to be charged before the cell would vent, divided by the rate of oxidation of these products. Because when these products are oxidized effectively oxygen is used, and allows the negative to charge as the other half of the reaction.

We proposed that this rate of oxidation is proportional to the polarization of the positive electrode, which is reasonable for a parasitic electrochemical process.

We propose, furthermore, that this rate constant follows the oreneous relationship shown here, and that the polarization follows a tophal relationship for an irreversible process. We can combine all of these factors into this equation, re-arranging the terms. And you can see that these

wb6

v..ues now are known: time to failure, the absolute temperature, the current density, and, again, temperature.

So if we plot the log of this factor versus one-over-T all of the data should be normalized. And, when in fact we do this, we get these results.

(Slide 30.)

The hexes, circles and squares are the three different charge currents, and there is no systematic arrangement of those charge currents in any of these four different temperatures. And the activation energy, again, by the way, is 14,15 kilocalories.

So we feel that the mechanism, then, is the hydrolysis of the nylon, these products then diffusing to the positive electrode, and then being oxidized electrochemically at the positive electrode a a rate determining step.

This mechanism is in agreement with data for cells containing only nylon separators. In that case the nylon is in contact with the positive electrode, so that the area of the reaction, the reaction site area, is equivalent to the size of the positive electrode. And one can normalize those data on the basis of the ampere hour capacity of the cell.

Art Cattotti at G.E. presented data of this type last year at the Electro-Chem Society meeting. And if you plot his data, which is expressed in terms of charge rate of

wb7

the negative per ampere hour cell capacity one gets a 14 to 15 kilocalorie per mol activation energy; again, in agreement.

(Slide 31.)

Now one can take these data, this mechanism, and conjure ways of extending the life of the cell under these conditions.

The first one, of course, is to eliminate all the nylon from the cell so that the mechanism cannot function.

One can also use a less reactive nylon, one which does not degrade in KOH as fast, so that you move the oxidation at the positive as a rate determining step to, perhaps, hydrolysis as rate determining.

You could make the path for diffusion of these products to the positive longer. And then that again would change the rate determining step probably, then, to diffusion control.

You could reduce the area of exposed nylon, or you could keep the nylon from wetting. So that this, again, would prevent the hydrolysis and change rate limiting step.

And then, of course, you could put in more excess cadmium hydroxide, up to a point; which just simply means that you take longer to charge the negative. In those cases you may run into problems such as resulting from carbonate build-up.

If you reduce the hydrolysis rate so that oxidation

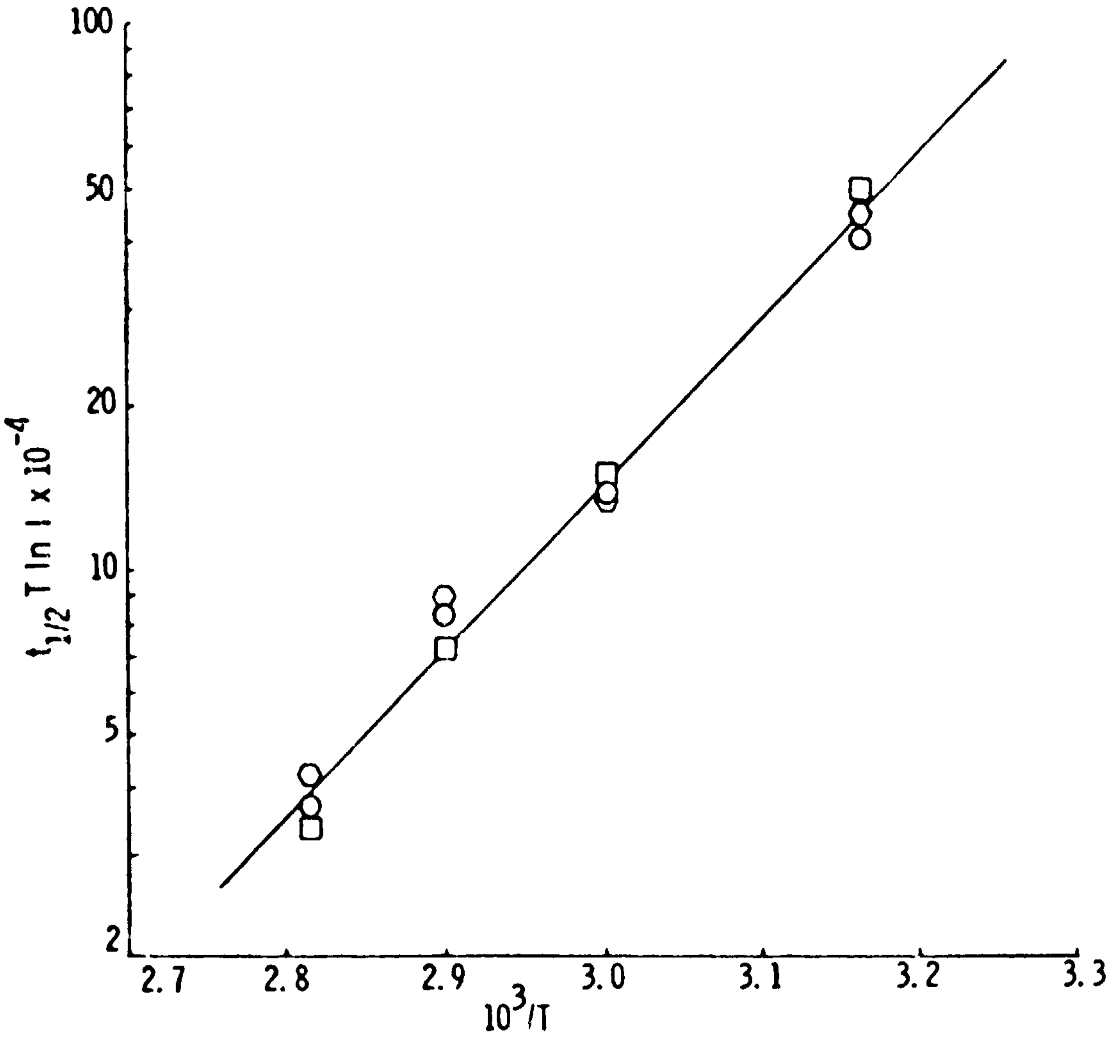

Figure 30

$$t_{1/2} = \frac{Q}{R_{ox}}$$

$$R_{ox} = k\eta$$

$$\eta = \frac{-RT}{\alpha nF} \ln I$$

$$k = k_0 e^{-\Delta E/RT}$$

$$t_{1/2}\ T \ln I = C\, e^{-\Delta E/RT}$$

Figure 29

RECOMMENDATIONS

1. ELIMINATE ALL NYLON.
2. USE LESS REACTIVE NYLON.
3. MAKE LONGER PATH FOR DIFFUSION OF NYLON DECOMPOSITION PRODUCTS.
4. REDUCE AREA OF EXPOSED NYLON.
5. KEEP GROMMET INSULATOR DRY.
6. MORE EXCESS $Cd(OH)_2$

Figure 31

wb8

of the products by the positive is no longer rate determining, one might very well run into the mechanism of oxidation of these decomposition products by oxygen in the cell. And we have some evidence being generated now that this is, in fact, the mechanism is some cells with polypropylene.

That's all I have.

HENNIGAN: Do we have any questions for Dean Maurer?

SCOTT: Will Scott, TRW. Were the hydrolysis products from nylon which were electrochemically oxidized identified?

MAURER: No, they weren't. As a matter of fact there's a whole series of them, and there is some evidence to indicate that the reaction rate with oxygen, for example, is different for the different chains that you might get.

SULKES: Sulkes, U.S. Army Electronics Command.

Is there a correlation with the weight loss of the nylon with, let's say, the amount of cadmium that would be available to react with the nylon? --with the oxygen that is generated?

MAURER: If one just does a mass balance, there is enough nylon present to account for all of the charging of the negative.

Is that what you mean?

SULKES: Yes.

Also, would there be enough that could react and

wb9

still maintain the physical integrity of the nylon? This would be the other thing.

MAURER: Well, that depends on how much excess negative there is. But in some of the cells that we have look at, the nylon still had its integrity, and would still serve its purpose.

The nylon in the area of the seal itself was not attacked at all. The insulator part, the part over the top of the core, was brittle.

SULKES: Thank you.

STEINHAUER: Steinhauer, Hughes. Dean, were these plates, or cells, that were used, of a standard impregnation process, or your new process that you have reported, or your lab has reported on previously, and would the effect, if these time constants you're reporting are dependent upon failure of the negative, would it be different, or would the rates or mechanism proposed be different in those cells?

MAURER: They were commercial cells with some modification. But the electrodes were prepared by commercial processes by a commercial manufacturer.

I don't think that the characteristic of the negative is of any particular significance here. I think it's simply a matter that the negative charges because there is no oxygen reaching it, or a small fraction of the oxygen that should get there is no, so it charges.

b10

Of course, depending on the type of negative it is, you might find some slight different charging characteristics or time to hydrogen evolution, let's say. In some negatives which perhaps have poor charging efficiency at the high charge levels you may run into hydrogen much sooner than you might expect.

But, other than that, I don't think it's critical.

GROSS: Sid Gross, Boeing.

Dean, what were the lowest temperatures that you took data at?

MAURER: The lowest temperature was 43°C., 110°F. The cells lasted there 400 to 500 days.

HENNIGAN: Thank you, Dean.

I have a couple of short announcements.

Will everybody please make sure they sign the attendance list, before lunch anyway.

And any speakers we have had, would you give your vu-graphs or slides or tables, and so forth, to Gerry Halpert so we can get them copied, and he'll give them back to you.

There are a couple more people who had some information on separators, but we'll just have to move along to the seal area, and maybe we can get back to that later.

We have several speakers on seals.

Bob Steinhauer, I wonder if you would mind being the first one.

wb11

We do have one comment on separators by Lou Belove.

BELOVE: I would like to suggest that to some of the earlier speakers on separators, polypropylene separators, that they mention in the reports the amount of electrolyte and the concentration of the electrolyte that was used in the cells that were on test.

HENNIGAN: We have all that. The cell I was talking about was 34 percent

BELOVE: And how much-- You see, there is--

HENNIGAN: The nylon separators were 26 cc's. Hercules I think was the same. The Kendall was slightly less.

BELOVE: Did you try various amounts of electrolyte?

HENNIGAN: No.

BELOVE: We found that this plays a part in the proper utilization of polypropylene in nickel-cadmium cells.

HENNIGAN: Thank you.

Bob Steinhauer on seals.

STEINHAUER: I would like to cover two subjects, one is observed failure modes in large sized seals, again related to our low earth orbit program where we are dealing with 50-ampere-hour seals, and then to discuss some work that has been done at Hughes on internal funding to develop a seal for nickel-cadmium space cells.

On our low earth orbit program we found that we

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wanted to evaluate several different types of seals, and it was a question of which ones were available.

The latter part is actually part my contribution, part Chuck Pierce and Sam Euler at the Hughes Electron Dynamics Division.

(Slide 32.)

We have observed considerable active metal penetration into the ceramics on these large sized seals. As I point out these observed failures I would like to propose a cause that I think most probable. In the case of the active metal penetration -- and these are on stress relief type of seals, or seals that use the outer circumferential surface to bond to, I believe that this failure is caused by an excessive time-temperature dwell during the actual braze flow operation.

We have found a separation of the braze joint from the ceramic in the region of the stress relief collar in the upper braze fillet. This could be caused by an excessive cooling rate following the flow of the brazed alloy, namely, even though these materials are reasonably well matched, the braze alloy is not, and there are differences in thermal expansion coefficients.

We have found fractures in the ceramic under the braze joint. These also can be caused by excessive cooling rates.

wb13

We have found voids in the braze alloy itself. Cooling rates, resulting in shrinking voids, and also inadequate dwell during that braze to remove the gas that is generated in some of these processes.

Recognize, of course, that we have a problem of too much dwell; too much cooling; not enough dwell. It has to be controlled properly.

(Slide 33.)

The types of defects that will be seen have to do with the separation in this area of the braze alloy from the ceramic, and also in an active metal penetration below this joint in this region into the ceramic that can cause some subsequent problems.

(Slide 34.)

We evaluated three different vendors' seals. These seals, to my knowledge, were all made by the same manufacturer. And the reason we started looking at these seals is that this is a 50-ampere-hour size cell. We had an unually high incidence of electrolyte leakage, namely, we had twelve cells from each of three manufacturers, and about half of these cells indicated leakage in phenolphthalein checks. Our usual incidence rate of leakers on space programs where we buy many more cells in the 200 to 400 cell category, has been typically less than half of 1 percent.

This is the separation of the braze alloy from the ceramic. You can see this pull-away. Second, you can

wb14

see this active metal under the braze alloy that has diffused into the ceramic. You have what amounts to a titanium enriched zone and intrinsic ceramic.

Also, this is the macrophotograph, the optics are such that this is a mirror image; in other words, this corresponds to this, and this corresponds to this, but optically they are reversed. (Indicating)

You can also notice some fracturing starting to propagate along this boundary between the titanium enriched material and intrinsic alumina, possibly started by this separation here, possibly in the cooling cycle.

This is typically a point of concern, Regardless of the type of metalizing you use, you do not want to get excessive penetration into the ceramic.

This photograph shows that, probably up in this region, a slight amount of titanium penetration, but not fracturing has developed; and this is relatively minor.

(Slide 35.)

All of these cross-sections were taken from cells that were identified as suspect leakers by chemical leak check.

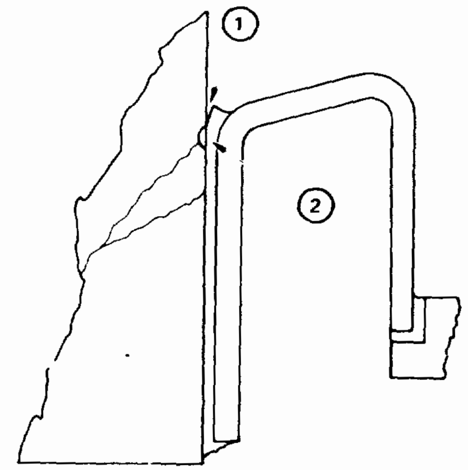
The cell just shown previously had a half-inch stud diameter. This was also on a 50-ampere-hour cell, but used approximately a quarter-inch stud diameter. This cross-section is not exactly through the center, or through a diameter.

OBSERVED FAILURES IN LARGE SIZE CERAMIC-TO-METAL TERMINAL SEAL AND THEIR PROBABLE CAUSE

OBSERVED FAILURE	PROBABLE CAUSE(S)
• ACTIVE METAL PENETRATION INTO CERAMIC	• EXCESSIVE TIME-TEMPERATURE DWELL DURING VACUUM BRAZE OPERATION
• SEPARATION OF BRAZE JOINT FROM CERAMIC IN REGION OF STRESS RELIEF COLLAR UPPER BRAZE FILLET	• EXCESSIVE COOLING RATE FOLLOWING FLOW OF BRAZE ALLOY
• FRACTURES IN CERAMIC UNDER BRAZE JOINT	• EXCESSIVE COOLING RESULTING IN SHRINKAGE FRACTURES
• VOIDS IN BRAZE ALLOY	• EXCESSIVE COOLING RATE FOLLOWING BRAZE FLOW RESULTING IN SHRINKAGE VOIDS • GAS POCKETS RESULTING FROM THERMAL DECOMPOSITION OF HYDRIDES, I.E., INSUFFICIENT TIME-TEMPERATURE DWELL DURING BRAZING, OR IMPROPERLY CLEANED PARTS.

Figure 32

FAILURES OBSERVED IN LARGE SIZE METAL-CERAMIC TERMINAL SEALS



1. SEPARATION OF B[illegible] ALLOY FROM EXCESSIVE COOLING RATE AND DIFFERENTIAL THERMAL EXPANSION FOLLOWING BRAZE ALLOY FLOW

2. TITANIUM ENRICHED ZONE IN ALUMINA CERAMIC – FRACTURE DEVELOPS IN BOUNDARY BETWEEN THE TITANIUM ENRICHED ALUMINA AND INTRINSIC ALUMINA

   CAUSE EXCESSIVE TIME TEMPERATURE DWELL DURING BRAZE PROCESS

Figure 33

METALLURGICAL CROSS SECTION OF THE NEGATIVE TERMINAL SEAL FROM EAGLE-PICHER CELL L1-9

Figure 34

METALLURGICAL CROSS SECTION OF THE NEGATIVE TERMINAL SEAL FROM EAGLE-PICHER CELL L1-20

Figure 35

57A

wb15

The defects noted in this seal were less. You can still see some separation, but it's not as defined. You can see some titanium penetration in here. This is fairly clean at the top. I could not find any actual fracturing.

In general, the seals with the smaller thermal mass exhibited fewer defects. I think that this is very significant in why we have not seen-- Any defects that we see in small size seals, I mean like 6 through 20-ampere-hour, will be magnified with a large thermal mass type seal.

This is why I believe the smaller stud diameter directly resulted in less observation of the problem there.

(Slide 36.)

This is another one with a half-inch stud diameter. Even in the macrophotograph you can see the fracturing which is a direct leak path. The blow-up of this shows that fracturing did occur at the top. There's a titanium enriched zone. But once you get this boundary line between the enriched zone and the intrinsic material, the fracturing started, that can act as a notch point, just like in glass, to propagate further fracturing.

This side you can see, which is here, that the braze alloy has separated from the ceramic. Further, some fracturing has occurred up in here, but it has not propagated on around.

wb16

(Slide 37.)

This one also had a half-inch stud diameter. We were somewhat concerned when we saw the tap on this hole and the distance between here and here. But it was not a leak path.

The separation has occurred here. The titanium has penetrated in this region.

Now with that separation, and with some penetration, if you look here you can see the separation, you can see the penetration zone on this one, but if you follow this right on down all the way down and through, it's a direct leak path.

(Slide 38.)

We have observed another, perhaps not failure mode but something that we ought to consider. Where we are using single insulated cells -- in other words, ceramic-metal seal on just the positive terminal, we have looked at the metal-to-metal braze between the stress relief collar and the cell cover.

We have found, in metallurgical cross-sectioning that there appears to be copper-rich zones of braze alloy apparently undergoing a deplating-plating process involving the copper. The path length of this particular braze is sufficiently long to preclude electrolyte leakage. The final location of this copper, some of it plates back on;what

wb17

doesn't quite make it, I'm not sure where it goes: I'm somewhat concerned.

The rate of attack is about .2 to .5 mil per year, because we have analyzed cells that we have had around one year, two years, and three years, in storage, in a strapped-out condition. And point that the polarity of this braze is negative.

It's of interest to note that where there has been a tendency of late to use organic materials, for one reason or another, on these seals, and that where the organic material covered this particular fillet there was no detectable corrosion or deplating.

(Slide 39.)

This is the braze that we're talking about, the cell cover. This is the stress relief collar going to the ceramic. And we're particularly concerned with this fillet. And it would have to propagate through this path length.

These are 150 and 250 power magnifications showing some of the rough surface that has been developed.

You might notice the gas pocket in this braze alloy.

(Slide 40.)

These will show the problem, still in the one year: I did not get a chance to get the three-year slides made up, but they look much the same. Only you can measure

METALLURGICAL CROSS SECTION OF THE POSITIVE TERMINAL SEAL FROM GULTON CELL L1-152

Figure 36

METALLURGICAL CROSS SECTION OF THE POSITIVE TERMINAL SEAL FROM GENERAL ELECTRIC CELL L01-006

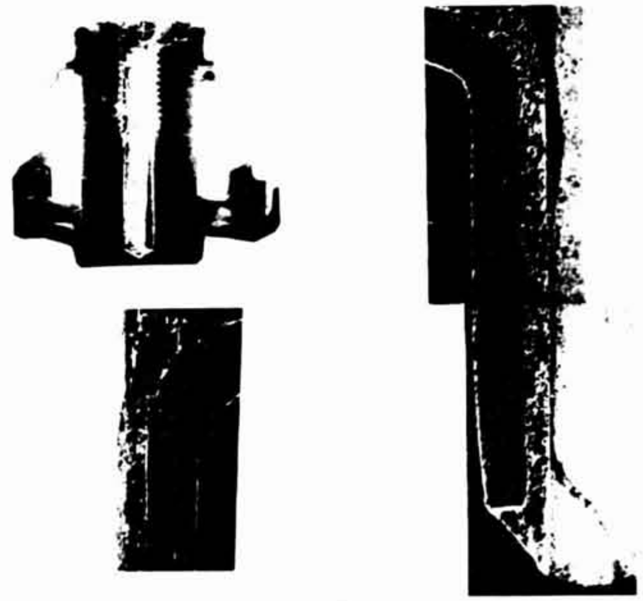


Figure 37

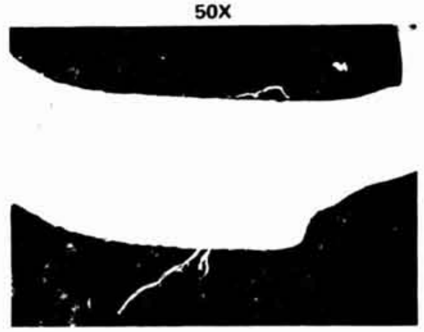
SINGLE POSITIVE CERAMIC-TO-METAL SEAL METAL-TO-METAL BRAZE ALLOY ATTACK

- COPPER RICH ZONES OF BRAZE ALLCY JOINING THE STRESS RELIEF COLLAR TO THE CELL COVER APPARENTLY UNDERGO A DEPLATING–PLATING PROCESS INVOLVING COPPER.
- PATH LENGTH PROBABLY IS SUFFICIENTLY LONG TO PRECLUDE ELECTROLYTE LEAKAGE.
- FINAL LOCATION OF COPPER UNDERGOING THIS DEPLATING–PLATING PROCESS IS NOT KNOWN, BUT COULD BE DISSOLUTION INTO CELL'S ELECTROLYTE.
- RATE OF ATTACK OF BRAZE FILLET IS IN THE RANGE OF 0.2 TO 0.5 MIL PER YEAR.
- POLARITY OF THIS BRAZE FILLET IS NEGATIVE.

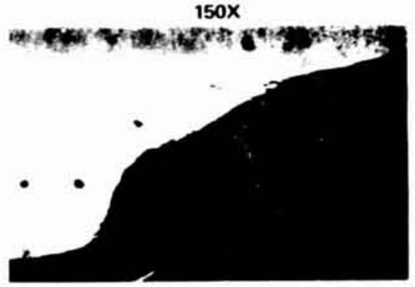
Figure 38

CELL NO. : 020-18

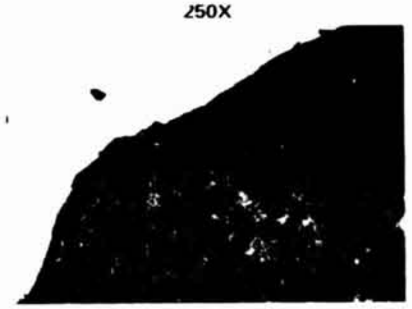
50X



150X



250X



COVER TO STRESS RELIEF COLLAR METAL TO METAL BRAZE. DEPLATING PLATING OF COPPER RICH ZONES IN PALCUSIL 5. APPROX 1 YEAR WET LIFE

Figure 39

wb18

about twice the depth, maybe. But you can see this corrosion that has developed.

This is an etched specimen. These darker regions appear to be copper-rich. This appears to deplate and follow these copper-rich zones. And then this material that you can see fragmented on the surface appears to be where the material has attempted to plate back onto this braze.

The question is: all of it didn't make it: where is it?

Another point I want to make: This is on a 15-ampere-hour cell. We were looking at the same cell for this phenomenon. To the eye, we didn't see anything wrong with it, but I had just gone through those 50's on this item that I talked about previously, and I said "Hm. I don't see anything, but let's flip the metalograph over here." And, sure enough, this same area shows no penetration but does show separation from the ceramic.

So we ought to be cognizant of that in smaller sized seals as well.

(Slide 41.)

We found recently a failure of several cells that had been in storage, namely that they failed this incipient short test. With extensive overcharge we were able to recover and to restore all but two cells.

In these two cells, which appeared to be a different failure mode, we took a look. These cells showed on autopsy spotting in localized regions of the separator, dark gray, black; they showed a lot of spotting on the positive plates, perhaps nickel oxide.

At any rate, I would like to point out what was found in analyzing the separators of these cells.

I haven't left ceramics, Tom, really.

Up here is the analysis of the ceramic body that was used in these cells, with alumina, silica, magnesia and so forth, across the top. These are all coded in red.

The items that I have coded in red below here I am attributing to the ceramic.

We took a background analysis, namely, the white portion of the separator versus the portions of the separator that exhibited black spots around periodically, and a black smear that appeared across the top of the separator.

You notice that the background analyses are fairly clean, except for things that you might expect. There is an absence of cadmium. These are cells that had been overcharged to a considerable extent. However, in the background here you see some traces of quite a few elements.

In these black spots especially, and to a lesser extent in the black smears, we found high concentrations of things such as silicon, magnesium, iron, calcium, potassium,

wb20

of course, sodium, titanium and nickel.

The nickel I attribute to the black spots, or the predominance of spotting on the positive plates.

I believe that the iron, in the case of this cell, the spot analyzed was directly adjacent to a pit in the positive plate that went down to the substrate material, or cold rolled steel.

I believe, after studying this and looking-- These last two, these are just a replot of the data, assuming these to be concentrations, and subtracting out backgrounds from this analysis and from this, to try and see what is significant. So we can probably just look down in here.

I believe that the nickel and/or the iron are acting as initiators to start drawing all these materials together, that these materials are indeed coming from the ceramic, and that the high -- once these two items start this process; and recognize that this was after long-term strapped storage; we get high silicon, we get high sodium, and high titanium. And to a lesser extent -- and this is kind of disturbing -- we get aluminum.

That kind of surprised me.

But I am proposing that we consider the ceramic we use with regard to whether it is indeed causing us cell failures by this mechanism.

I think further work has to be done to identify

wb21

the compounds and to identify the stoichiometry, and so forth.

(Slide 42.)

The conclusions from this: I think there is a correlation between the fluxing agents of the ceramic and the high concentrations in the suspect region of the separator. I think that nickel that has moved out -- not sintered, but probably starting from impregnated materials, has moved out, and is one of the initiators of the mechanism. I think iron can be another, from the substrate.

Of course we could put a lot of numbers in front of each of these, but I think that's a-- You know, these compounds, except for the nickel, occur in nature. I think that something like that is probably going on.

I think we have to consider what it really means, pits, cracks, and so forth, especially in the positive plates, because of this iron, down to the substrate. I think that this is probably an initiator of this failure mode. And I think that the external short circuit long-term storage of cells should be reviewed as perhaps causing this nickel to move out into the separator.

Those are the observed failures.

I would like to now go into the second portion that covers the seal that was developed by Chuck Pierce, Sam Euler and myself, reduced to practice down at the Hughes Torrance Division. We do have a patent applied for on this.

wb22

This is using technology that they have developed on pin seals for microwave tube windows.

The technology was available there. I used to be involved with that Division and with their metal ceramics, which is why I saw a need to perhaps go to the tube people and say "Gee, we have a special requirement. I know what your capabilities are." There was just not enough translation between battery and seal people.

(Slide 43.)

This is the Hughes Hi-Rel seal. We picked that name for lack of a better one. It does not use silver in the braze alloys. It uses butt-seal geometry, which has been around long before we had space nickel-cadmium cells, used in the tube field for klystrons, biwows, PWT's, in the gun structures especially. It uses a braze temperature of less than a 1000 C. And the reason I point that out is that the time-temperature dwell on those failures shown previously, it is critical. If you go to higher temperature you're going to get greater penetration in a shorter time.

We're talking about high alumina, 99.8 to 99.9, a minimizing the silica. I feel that the silica is one of the main components in there leading to that short through the separator.

It uses the back-up ceramic rings, which seem to have no purpose in the seal itself. They seem superfluous, l

CELL NO.: 020-18

50X

METAL-CERAMIC BRAZE AT STRESS RELIEF COLLAR.

NOTE SEPARATION OF BRAZE ALLOY FROM CERAMIC – PROBABLY CAUSED BY EXCESSIVE COOLING RATE FOLLOWING BRAZE FLOW

150X

COVER-TO-STRESS RELIEF COLLAR METAL-TO-METAL BRAZE.

250X

DEPLATING PLATING OF COPPER RICH ZONES IN PALCUSIL 5. CELL APPROX 1-YEAR WET LIFE

Figure 40

TYPICAL TERMINAL SEAL CERAMIC COMPOSITION AND SEMI-QUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSIS OF SEPARATORS FROM CELLS 60-08 AND 80-01

	Al_2O_3	SiO_2	MgO	Fe_2O_3	CaO	K_2O	Na_2O	TiO_2
AMERICAN LAVA 614	95.9	2.8	0.9	0.1	0.14	0.03	0.1	0.05

	Al	Si	Mg	Fe	Ca	K	Na	Ti	Ni	Cu	Li	Cr	Co	Cd	Mn	Ag	Mo
HS 223 SEPARATOR S/N 60-08 BACKGROUND						56	0.15		0.007		0.005						
HS 223 SEPARATOR S/N 60-08 BLK SPOTS	0.01	0.67	0.53	0.2	0.03	53	0.51	[illegible]	0.43			0.006	0.004		[illegible]		
HS 223 SEPARATOR S/N 60-08 BLK SMEAR	0.002	0.03	0.003	0.04	0.004	56	0.12	0.08	0.2	0.01		0.006					
HS 223 SEPARATOR S/N 80-01 BACKGROUND	0.001	0.01	0.003	0.003	0.001	56	0.11	0.01	0.03	0.001	0.009						
HS 223 SEPARATOR S/N 80-01 BLK SPOT	0.18	0.2	0.03	0.47	0.13	48	4.1	0.17	1.3			0.01	0.02			0.04	0.16
HS 223 SEPARATOR S/N 80-01 BLK SMEAR	0.002	0.04	0.005	0.004		57	0.13	0.008	0.03	0.005	0.009						
HS 223 S/N 60-08 SPOTS BACK	0.01	0.67	0.53	0.2	0.03	3	0.36	0.3	0.42		0.005	0.006	0.004		0.006		
HS 223 S/N 60-08 SMEAR BACK	0.002	0.03	0.003	0.04	0.004	0	0.03	0.08	0.2	<0.01	0.005	0.006					
HS 223 S/N 80-01 SPOTS BACK	0.18	0.19	0.027	0.47	0.13	8	4.0	0.16	1.3	0.001	0.009	0.03	0.02			0.04	0.16
HS 223 S/N 80-01 SMEAR BACK	0.001	0.03	0.002	0.001	0.001	1	0.02	0.002	0	0.004	0						

NOTE: ALL ELEMENTS AND COMPOUNDS REPORTED IN WEIGHT PERCENT

Figure 41

TENTATIVE CONCLUSIONS REGARDING THE FAILURE MECHANISM OF CELLS 60-08 AND 80-01 FOLLOWING ONE TO THREE YEARS STORAGE IN SHORT CIRCUIT CONDITION.

- APPARENT POSITIVE CORRELATION BETWEEN TERMINAL SEAL'S CERAMIC FLUXING AGENTS AND ELEMENTS FOUND IN HIGH CONCENTRATIONS IN SUSPECT AREAS OF SEPARATOR.
- NICKEL (PROBABLY ACTIVE NICKEL) IS ONE OF THE INITIATORS OF THIS FAILURE MECHANISM.
- IRON FROM POSITIVE PLATE SUBSTRATE ALSO IS A SUSPECT INITIATOR.
- PROBABLY A COMPLEX CONDUCTIVE COMPOUND IS FORMED LOCALLY IN THE SEPARATOR, SUCH AS:

$$Na_2O \cdot K_2O \cdot Al_2O_3 \cdot Fe_2O_3 \cdot CaO \cdot MgO \cdot TiO_2 \cdot SiO_2 \cdot NiO \cdot nH_2O$$

- PITS, CRACKS OR OTHER DEFECTS, ESPECIALLY IN POSITIVE PLATES DOWN TO COLD ROLL STEEL SUBSTRATE MATERIAL, ARE UNDESIRABLE.
- SURFACE NiO OR $NiO \cdot H_2O$ IN THE FORM OF BLACK SPOTS OR PATCHES ON THE SURFACE OF POSITIVE PLATES IS UNDESIRABLE.
- EXTERNAL SHORT CIRCUIT STORAGE OF CELLS MAY BE A CONTRIBUTING FACTOR IN THIS FAILURE MECHANISM.

Figure 42

HUGHES HI-REL SEAL

- NO SILVER USED IN ANY BRAZE ALLOYS
- USES BUTT SEAL GEOMETRY
- BRAZE TEMPERATURE < 1000 °C
- 99.8 TO 99.9 WEIGHT PERCENT ALUMINA WITH <50 PPM SILICA
- USES BACKUP CERAMIC RINGS TO ENHANCE TENSILE STRENGTH BY 1.5 TO 2.0X
- ACTIVE METAL IS DIRECTLY DEPOSITED ONTO CERAMIC
- ALL MATERIALS ARE COMPATIBLE WITH NICKEL CADMIUM CELL CHEMISTRY AND ELECTROCHEMISTRY. ALL HAVE BEEN USED IN Ni/Cd CELLS PREVIOUSLY ALTHOUGH NOT NECESSARILY IN THE SEAL.
- 12-17K PSI YIELD STRENGTH DEPENDENT UPON CERAMIC USED.
- PROVEN MANUFACTURING PROCESS FOR LARGE SIZE SEALS
- ALL MATERIALS INDIVIDUALLY TESTED FOR COMPATIBILITY WITH CELL'S INTERNAL ENVIRONMENT

Figure 43

they actually act as a sandwich or a strengthening factor because the metal that is sandwiched in between does not exactly match the expansion of the ceramic, and you do not want to use thick metal because this would just make the joint more rigid.

So this does indeed enhance the tensile strength. That is measurable.

We deposit active metal directly onto the ceramic rather than to convert it from a compound.

All the metals have been used in nickel-cadmium cells and are compatible. They have not all necessarily been used in the seal before.

In a tensile specimen yield strength test -- I'm not inferring that the actual structure would give this tensile strength -- it gives 12 to 17 thousand psi at yield. The actual structure--we've tested some of the earlier specimens for which we had not developed our appropriate cooling cycle at that time -- showed around three and a half to four on the actual structure. --K, of course.

I'm saying that large size seals really are the proof of the pudding. If you can make a large one, then you can make a small one. The reverse is not necessarily true.

All the materials have been individually tested by an electrolytic corrosion test described to me by Dr. Seiger of Heliotek for compatibility in the cell's

wb24

environment.

Sid Gross just commented to me before I came up here that perhaps this test should be repeated with actual electrolyte from the cell; that trace impurities in the electrolyte -- I recognized in the titanium; but in the electrolyte -- could have an effect on these corrosion results.

(Slide 44.)

When I asked to get this work released I said I would either present it or not, depending upon whether I could talk about the metallurgy. And they did go ahead and release it. This is what it is.

Right now we're using a Wesco 998 body. We went to Coors, but it is difficult to get that body from Coors and -- lead time. And it is much more expensive from them than to use this body.

The Wesco body contains less than 50 ppm of silica as does the Coors body.

It is an RF sputtered titanium for the active metal. And, as such, it is extremely thin compared to what we're used to in these seals. That's important in that you don't have a big reservoir of that to move into the ceramic.

It makes use of a platinum barrier layer. That's for two purposes. One is to protect that titanium once you bring it out of the vacuum system, and, second, to keep this material from alloying extensively with the nickel-gold, which will form a beautiful ternary, at least a binary, the titanium-nickel, and the titanium will be drawn into gold as well.

It does make use of iron-nickel-cobalt, or ASTM F15 alloy,, which is a low expansion. It's slightly different from the alloy 52 which has been used in seals to date. But cobalt I do not find objectionable.

This could be made with the alloy 52 as well. It's just that we feel this has a better match to the ceramic.

It could possibly be made with nickel-metal, but you have a gross difference in expansion there, and you are incurring a higher risk.

It makes useof the nickel 200 stud.

(Slide 45.)

I have a cross-section of the seal with me, and I will have a photograph of it if anyone cares to look at it later.

This is one of the back-up ceramic rings on the top. This is the other one underneath. It is the butt-seal geometry, or what I have referred to in the past as electron gun geometry.

There is a metal-to-metal braze between the post and this ring here.

This is one of the tensile specimens that we measured that 12 to 17 thousand psi on. This was based upon the area that you see. The important part is that it is indeed pulling ceramic. And this was one of the earlier runs. Presently we pull ceramic-- There is ceramic in these areas, but it is extremely thin. It looks in this photograph as if it's not there, but there is ceramic completely around.

In some cases it is not good to pull ceramic if you have an active metal enrichment; you have embrittled your ceramic.

(Slide 46.)

This is the cross-section showing the stud: the one member of alloy F15, a metal-to-metal braze at this point, back-up ring, back-up ring, stand-off ceramic, and then the metal-ceramic brazes affecting the seal, being these two on either side. And then that metao-to-metal one.

This has not been put into a collar. This could either be tig-welded in or brazed in.

The bond metallurgy at low power -- and these are etched specimens: this is ceramic, ceramic, and by going across in this region here you can see the F15 alloy, the braze alloy and the ceramic. And likewise above.

The titanium and platinum are along this interface. I'm not sure you'll be able to see this from the back of the room, but even in this photograph you can start to see the very thin titanium. And this is at very high power, much higher power, at least two times here, than what those defects were shown at before.

There is essentially surface bonding, but no penetration into the ceramic.

At the higher power you can see the titanium surface bonfing right on the crystalline structure of the ceramic. You can see a slight layer here. And then there's another one here. This is braze alloy of nickel-gold, eutectic nickel-gold.

This is the platinum layer that you can see running along through here.

This type of seal I think is one that should be looked at, because you do not get this penetration. It can be made in a large size.

(Slide 47.)

This is the same metallurgy but in an unetched specimen. And the only difference is that you can see the titanium, or the lack of penetration, and in the interface here you cannot detect the barrier layer.

We developed this seal because of our obligation on the low earth orbit program to evaluate several different seals. This used previously developed technology at Hughes.

There is one other seal that we find interesting. This has been developed by General Electric at their Schenectady Microwave Tube Business Center, which, coincidentally

HUGHES HI-REL SEAL METALLURGY

- HIGH ALUMINA CERAMIC – $\geq$99.8 TO 99.9 WEIGHT PERCENT Al_2O_3
 $<$50 PPM SiO_2
- RF SPUTTERED TITANIUM (ACTIVE METAL)
- RF SPUTTERED PLATINUM (BARRIER METAL)
- EUTECTIC NICKEL-GOLD (BRAZE ALLOY)
- IRON-NICKEL-COBALT (LOW EXPANSION ASTM F-15 ALLOY)
- NICKEL 200 STUD

Figure 44

HUGHES HI-REL SEAL

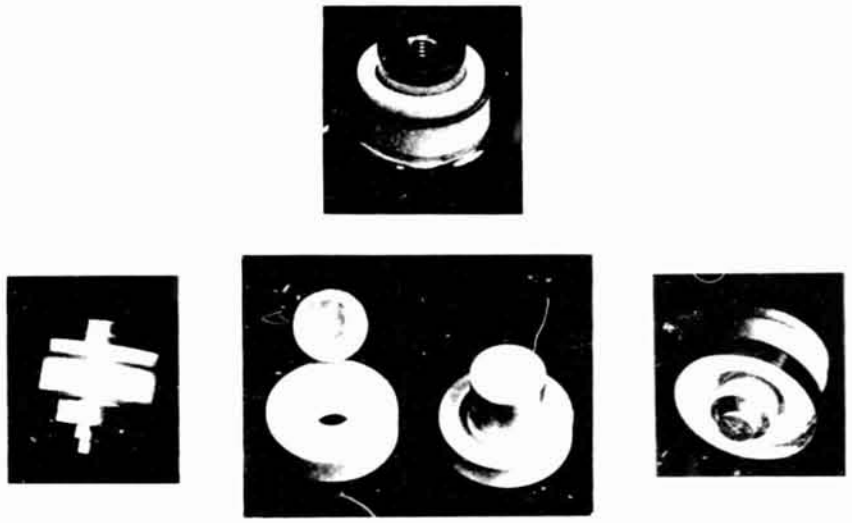


Figure 45

HUGHES HI-REL 50 AH METAL-CERAMIC TERMINAL SEAL

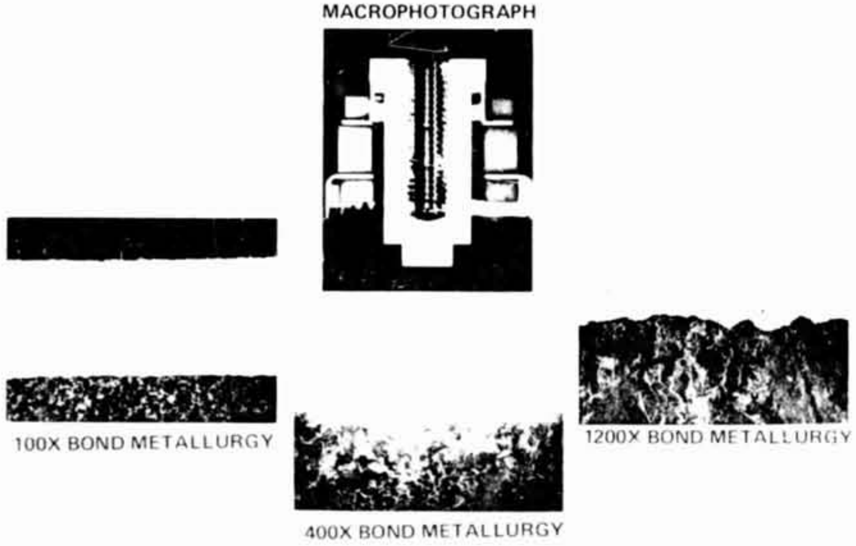


Figure 46

HUGHES' METAL-CERAMIC SEAL INTERFACE FOR ALKALINE CELLS

8/17/71
400 X

Figure 47

happens to be the competition to the division that did our work.

(Slide 48.)

This does not show penetration of the active metal into the ceramic. However the seal that I have here is only a 6-ampere-hour size. I would be very interested in seeing something that gets up in the stud diameter of about half an inch.

They are using a braze, as you can see from the fillet here.

I am concerned in that I want to see a large sized seal, and if that same metallurgy exists it is definitely promising. And my reservation is the following:

This must be brazed at a much higher temperature, it is my understanding. Therefore the time-temperature dwell in that process appears to me to be more critical a process parameter than the lower temperature of the seal I have just described.

From what I can see, for large sized seals, or for long-life high-reliability seals, I would like to see others, but these are the two that I find promising at the moment.

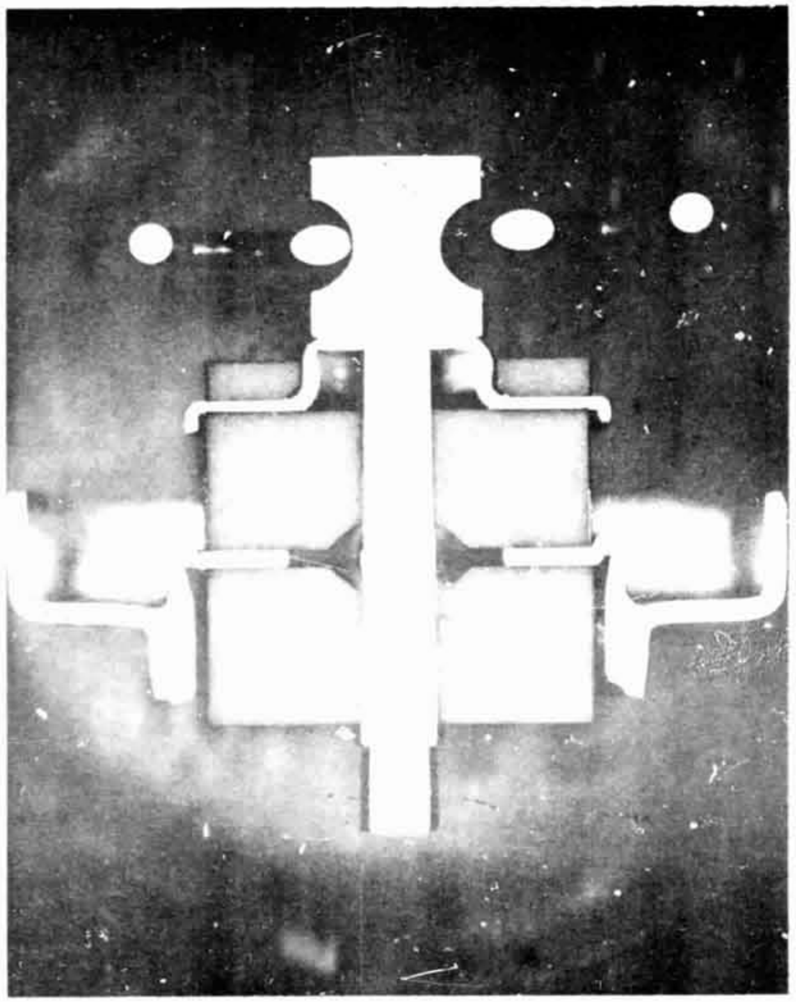
HENNIGAN: Do we have any questions of Mr. Steinhauer?

KRAUSE: Stan Krause, JPL.

Bob, how old were these cells, the original ones

G.E. BONDLEY SEAL 6AH

MACROPHOTOGRAPH



800X BOND METALLURGY

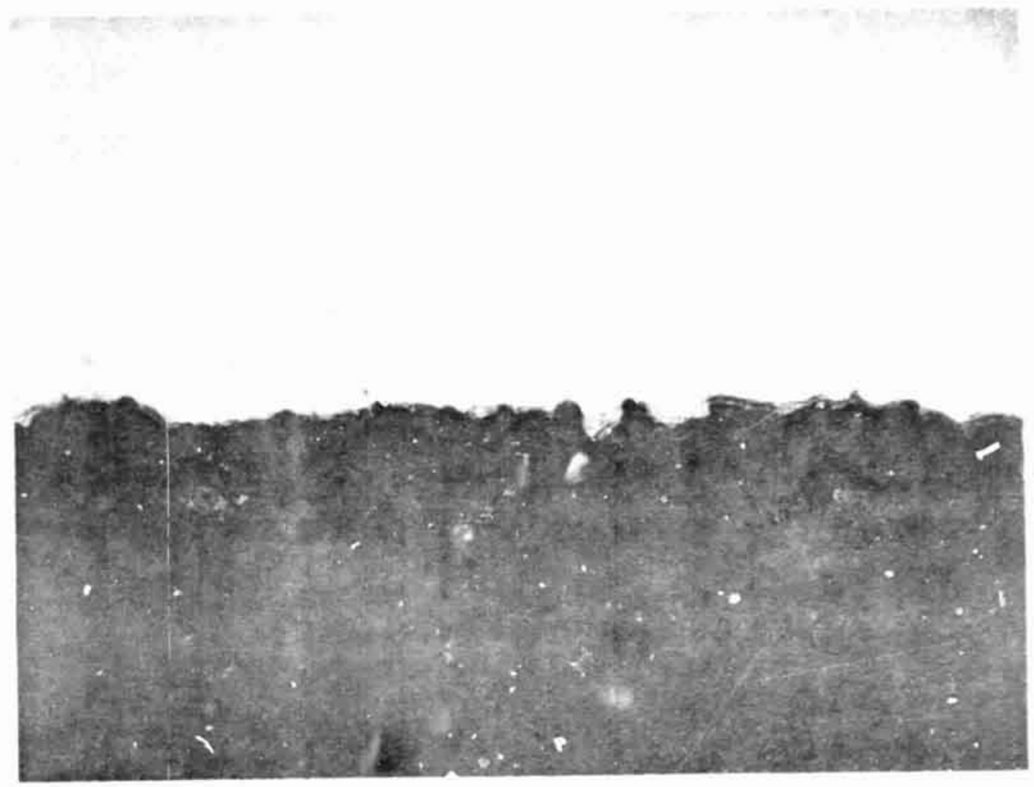


Figure 48

wb29

in which you detected some of those defects? How old were they when you found those leaks, and what had been done to them prior to discovering those leaks.

STEINHAUER: Of the large size cells?

KRAUSE: Yes. The first ones you talked about.

STEINHAUER: Yes. Those cells were observed to be leaking almost immediately upon receipt at Hughes.

We studied them for several weeks to several months before deciding whether they were actually leakers. They were not profuse leakers; just give small indications, in most cases, of reaction to phenolphthalein.

You have to be careful before you go in and cross-section one of these things, because if you don't hit the right spot you'll never know what you have. Therefore we studied them for quite a few weeks to -- maybe up to three months, to determine where to cross-section. So they were no more than three months old after receipt at Hughes.

KRAUSE: Has it been your experience that leakers, as a result of seal manufacturing defects, show up very early in the life of a cell?

STEINHAUER: I assume you are now referring to a smaller size seal. --or just in general. Let me comment in general.

In our space programs we have found this .5 percent of leakage incidence usually within -- starts showing up three

wb30

months to six months after receipt from the cell manufacturer. The frequency seems to be that they peak out within that time. You don't find them before, you don't find them after.

That has been our experience. Except on these large size seals.

GASTON: On the Hughes type seal, do you plan to build cells and evaluate this seal on large sized terminals?

STEINHAUER: We, as you know, are not a cell manufacturer. We would plan to build seals for anyone who would care to incorporate them into cells.

We have limited capability at the moment. And, depending upon the interest, they would upgrade this to be able to handle larger quantities.

But the two people that I mentioned -- Sam Euler especially -- would be the main focal point persons to call if one were interested in pursuing this further. I can give you the number later.

COHN: Cohn, NASA Headquarters. On your own seal which is made with alumina, I would be interested in knowing which type of alumina, alpha or gamma, and whether you control the crystal form and whether you know whether there is an effect or whether it's one or the other.

STEINHAUER: I can't answer that, because we do purchase the body. I would have to find out.

There was no attempt to control it, no. It's a

wb31

commercial body.

FORD: Floyd Ford, Goddard Space Center.

Bob, in a few of your slides you showed some data that implied, the way I interpreted it, that the seal is degrading on the cell even though the cell is in storage and shorted out. Is this correct?

STEINHAUER: In the case of the deplating/plating, yes.

FORD: You mentioned the copper had a potential associated with it. And if these are single ceramic seals, I'm missing the point to understand how they can be shorted out.

STEINHAUER: They are externally shorted. I don't know what the resistance is.

I'm saying when that cell is operative it's in a negative polarity.

LACKNER: Lackner, Canadian Defense Research.

You mentioned that for penetration of the ceramic the time-temperature dwell was important. What order of magnitude are you talking about in minutes or seconds?

STEINHAUER: Usually these brazes are made by progressing the stacked structure that you're going to be brazing up to temperature slowly, getting it just below the flow point, and then taking it up to temperature, allowing it to flow, and bringing it back down.

That dwell typically can be of the order of seconds to maybe up to five or six minutes.

LACKNER: Does this mean that if it's over five or six minutes it's bad?

STEINHAUER: Its time and its temperature -- I mean it has to be specific to the equipment that's used, the hardware that you're trying to braze together, the braze alloy; in other words, what temperature: the time is more critical if you go to a higher temperature braze than if it is a lower temperature braze.

I'm saying it depends upon the part you're trying to build, the equipment you have to build it with, and the metallurgy that you're using.

LACKNER: I still am trying to find out what the order of magnitude was. What is bad? Two hours? Two minutes? Twice the length of time? Half the length of time? Or is it so specific that you can't pin it down?

STEINHAUER: I have not identified, because, of course, I do not have access to the process information for the particular seals we have cross-sectioned here. So I don't have a family of these things at different dwells to say just where it becomes critical. I really can't answer that that specifically.

HENNIGAN: If we have any more questions we'll get them after the next speaker. The next fellow may not be able to come back this afternoon, and he has some information on the General Electric seal that Bob just talked about, as far as test data and how it held up under cycling tests.

John Park, from the Goddard Space Flight Center Materials Group.

HENNIGAN: I would like to remind you all again, before you leave please sign the attendance list, and to get your slides or art work to Gerry Halpert so we can get it reproduced and get it back to you. There is a Xerox in this building, so we can get it done pretty fast.

PARK: I felt that there was a very unusual and unexpected correlation between the samples that I have and the previous speaker, because it just happens that Tom Hennigan did have one of the G. E. seals, and we did happen to look at it at about the same time. So we will take a look at one of those first.

To refresh your memory, I have here a photo of the G.E. seal as cut.

(Slide 49.)

I believe you can make it out here.

This is the top of it. The sectioning was with a diamond wheel. You have a sort of cap up here, but there is a braze between the metal and the ceramic. This is hollow in here, obviously, for the post to continue down. And there is a braze between the ceramic here and wb 34

the metal and the ceramic. There is a stress relief over here. There is also a braze right in here.

This particular one, as indicated, is the way it looks new.

(Slide 50.)

This is in a more polished condition, but I believe it's a little bit more apparent as to the way it is made.

There is, right there, a braze between the ceramic and the metal. And here is the ceramic, here's ceramic. This is the electrical connection inside the cell.

I do have some micros of the area right in here, which is a braze area.

(Slide 51.)

For your information, this is called the No. 041, and it has been used. It was operated at 20°C, at 25 percent depth of discharge, 2300 cycles. This is data that I received from Tom Hennigan.

This is the braze area, and I'm showing it only because there are really no flaws in it. As indicated, this has not failed. We kept looking for cracks, pits, gas holes, or whatever might be there; but we found nothing.

So this one looked real good.

(Slide 52.)

This might indicate the penetration of the active metal into the ceramic. This is at a 500X magnification.

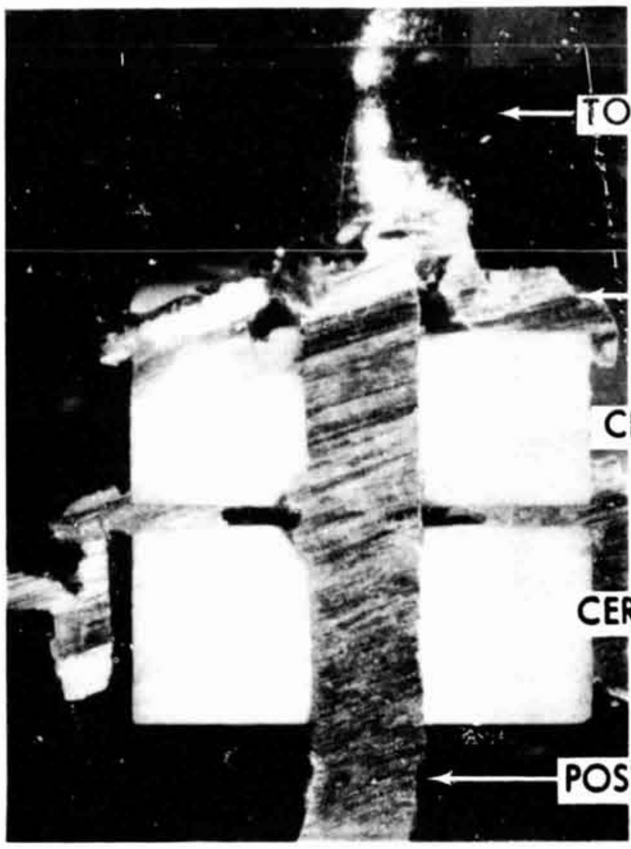


Figure 49.

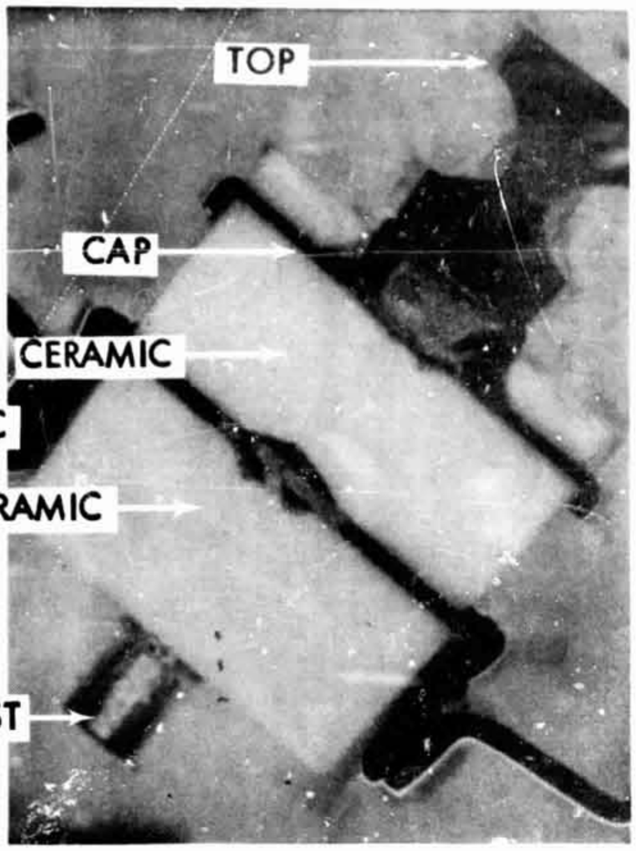


Figure 50.

Figure 51.

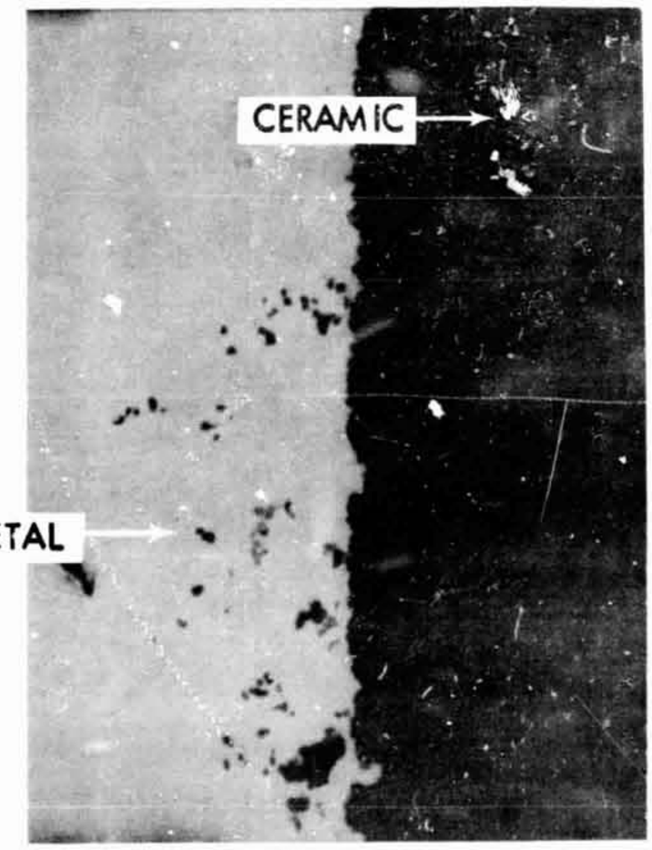


Figure 52

wb35

Here is your ceramic here, and your metal here. Presumably the metal-to-ceramic seal is right along here. We did not examine these areas in here, but it's obvious from what the previous speaker said that this is of interest. So we will take a look at these when we have a chance, like maybe tomorrow.

(Slide 53.)

This is an entirely different seal. And I bring this out, too, because again this has not failed. It's one received from Floyd Ford, it was given the number 866, and Floyd will give you the other details about it.

But, as indicated, this is a ceramic collar. The lines along here indicate where it is hollow, would normally be hollow. You have a stress relief collar up here. Here's the top of your header. There is a joint obviously right along in there. There is also a joint right in there.

This also has a seal down at the bottom in this general area here. But, as I said, it is hollow and goes through the middle.

(Slide 54.)

This is an upside-down picture, a little bit clearer, of the polished material. The ceramic is the white area here. As I said, it's upside down. So here's your stress relief collar going this way, and the joint, the brazed area,

wb36

right in there. Also in there. (Indicating)

(Slide 55.)

As I said, we were looking for flaws. It was not easy to find them. But at this 500X magnification you can barely make out something in this general area right in here, which is a crack. We do have it at a higher magnification, but there did seem to be an area right in this region that was going to develop into a crack.

(Slide 56.)

I think this is clearer, and it does show --this is at 1000X -- that there is a crack right in this region.

As I said, we did have to look fairly hard to find this. And as of now this is the only flaw we have seen in there.

I would like to ask Floyd now to give you any more details on this particular 866.

FORD: The particular seal that John has just showed you came off an OAO 20-ampere-hour cell, which is a Gulton-type cell. It had been tested at Goddard for just over 6000 cycles at 15 percent depth of discharge. It had seen a total operating life of about a year and a half.

It showed no indications of electrolyte leakage by the chemical leak test during this time period.

PARK: So it appears as though, at least in this

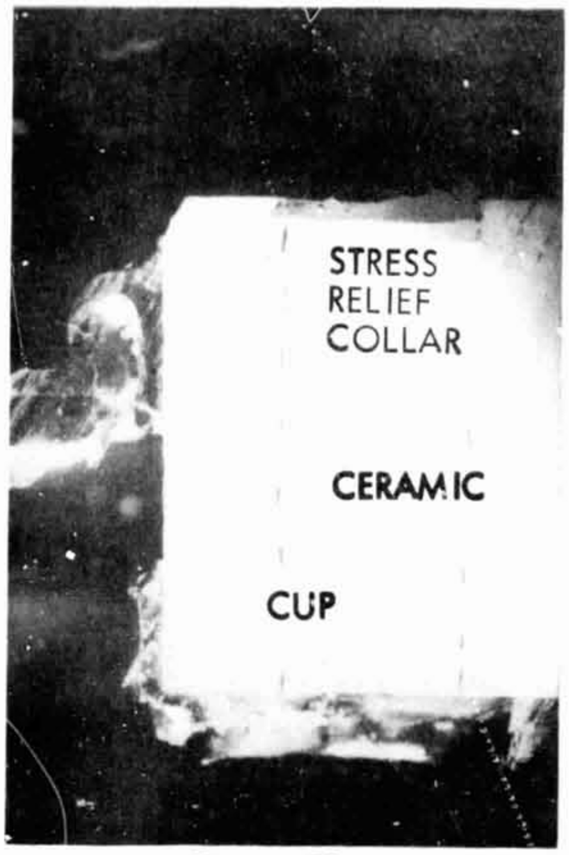


Figure 53.

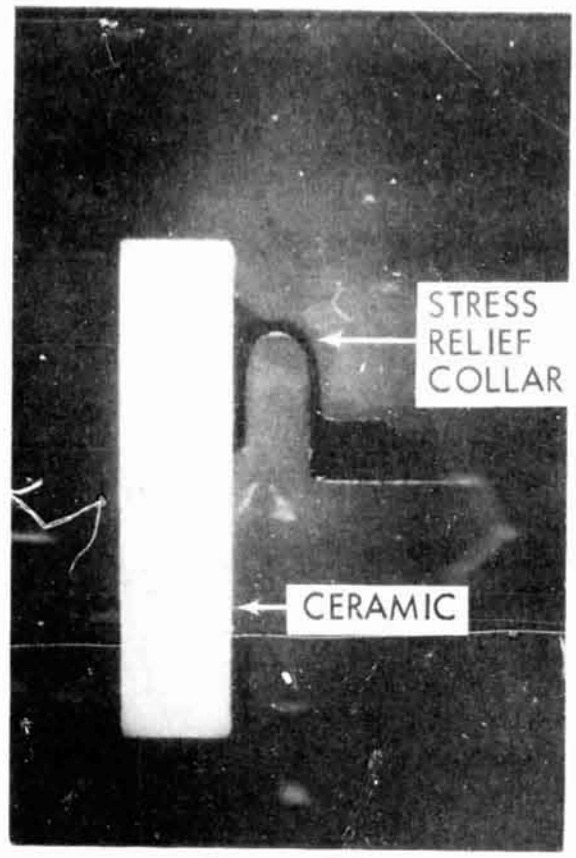


Figure 54.

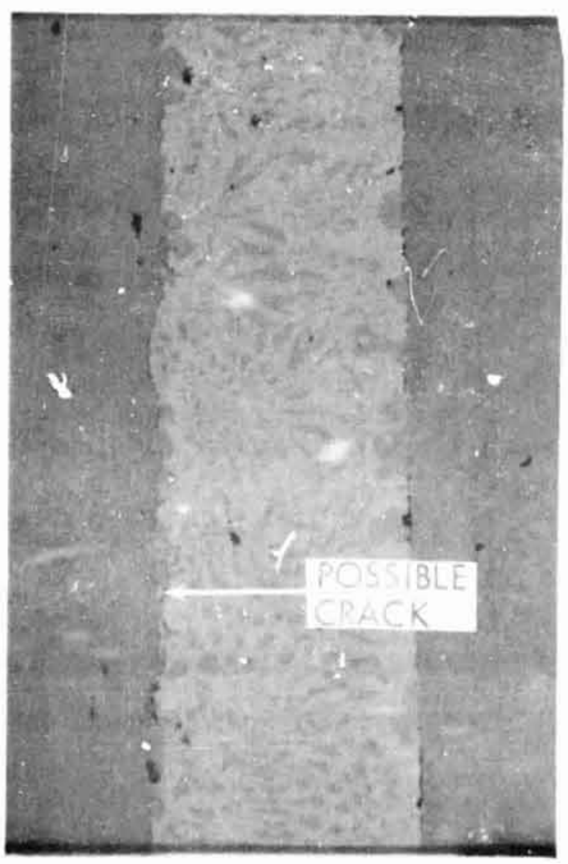


Figure 55.

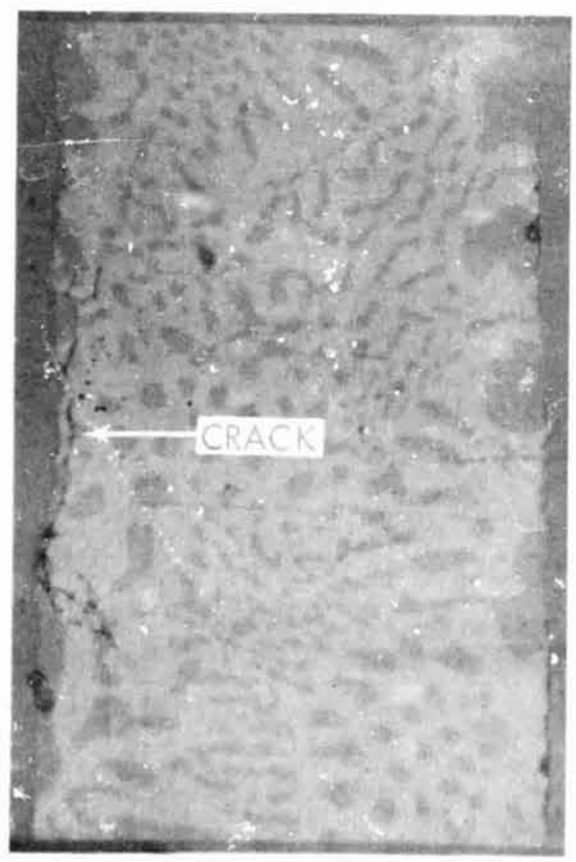


Figure 56.

wb37

particular instance, that we have found two particular different types of seals. And in this particular instance, again, none of these were failures, including the one at 25C., of G.E., or the 40°C. G.E. test, or the one that Floyd Ford just mentioned, from Gulton.

Are there any questions?

HENNIGAN: Well, if there are no questions we had better break for lunch. We're supposed to be there at twelve-thirty. It's kind of confusing to get over to Building 21, so perhaps we'd best follow each other.

Would everybody please come back at one-fifteen.

(Whereupon, a luncheon recess was taken.)

ebl
#3

AFTERNOON SESSION

(1:15 p.m.)

HENNIGAN: This will be a continuation of seals.

Our first speaker this afternoon will be Dr. Will Scott of TRW on their seal program.

xzxzx

SCOTT: Since the stated subject of this symposium is seals for large cells, I am going to confine my remarks to our experience with seals on large cells or something relevant to that.

We have had a program in-house for approximately two and a half years now involving batteries containing either 50 or 100 ampere hour size cells. In April of last year we purchased twenty 50 ampere hour cells from General Electric with two insulated terminals each. The terminal design of the manufacturer was that of Ceramaceal and the design was of the type that has been shown here already, which involves the placing of the ceramic-to-metal joints on the outside diameter of a cylindrical ceramic insulator.

I will show you a photograph, if you're not familiar with this, in a minute of the type that we actually have.

These twenty 50 ampere hour cells-- Oh, I should mention that about the same time we purchased three 100 ampere hour cells with the same size type and manufacture of terminal seal as on the 50's.

This terminal has about approximately a half-inch

eb2

diameter stud and the ceramic is three-quarters of an inch in outside diameter.

These cells have been on test in one way or another essentially continuously from that purchase date to the present time. When we initially tested them on receipt, they showed no indication of leakage as indicated by a phenolphthalein leak check. We did not do any kind of helium leak testing in-house although that testing had been done-- They had successfully passed that kind of tests at the manufacturer.

During the test program we checked them with phenolphthalein at intervals of about six months. After about a year we saw one cell with one indication -- one of the terminals indicating a very light leakage as indicated by a red phenolphthalein test.

Not long after that, one terminal on one of the 100 ampere hour cells just simply gave way, and I'll show you what I mean by that in a minute, and the cell vented and as we expected, a leak test on that cell showed a great big bloody mess around that terminal.

At that point which was, I guess, about three months after -- about fifteen months along in the life of the cells, we again tested all the rest of the cells. Since we had the bottle of phenolphthalein out, we just thought it would be a good idea to use it. And lo and behold, at that time

eb3

there was positive leakage indication on five of the 50 ampere hour cells. In each case, the leakage was at one of the ceramic-to-metal braze joints and interestingly enough, in every case it was on the negative terminal.

I don't know what the real interpretation of that point is as yet but it is interesting.

This includes the failure of the terminal on the 100 ampere hour cell. That was also on the negative terminal.

At that time we took the 100 ampere hour cell apart and did a more detailed examination of the terminal. We also took one of the 50 ampere hour cells apart and did some metallurgical sectioning and examination on that.

About that time we were aware of some of the things that Bob Steinhauer was saying this morning in terms of possible failure mechanisms for these large seals so we were looking for some of the things that he had seen in the terminals that we had.

I want to show you some photographs now of the terminals as they were when they were new and of the one terminal which failed and I'll make a few more comments on that.

(Slide 57.)

This is a photograph of the type of terminal seal we're talking about before it is installed onto a cell.

eb4

(Slide 58.)

This is a photograph of the terminal on the 100 ampere hour cell, the external appearance. This photograph was obvious taken after the cover had been removed from the cell. You can see a crack runing vertically from the upper to the lower metal part there.

There were actually three of those cracks around the circumference of the insulator at the time when we took the cell apart and as you will see in a minute, there was a hidden crack that isn't obvious from this photograph, also.

This is a polished cross-section --

(Slide 59.)

-- of that same terminal and it shows the hidden crack I was talking about, namely, the crack extending from the outside of the upper flange directly radially into the inside of the insulator. And that crack was in a plane perpendicular to the axis of the stud and went completely around the terminal.

Now it isn't apparent from this photograph but in the course of assembling these cells, all of -- I won't say "all" but most of the internal void volume of this terminal assembly was filled with an epoxy resin compound. Actually the method of doing that is to invert the direction of the cell turned upside down and filled to a certain level with the epoxy resin.

In this case we saw that the resin had flowed all

eb5

the way up the small space between the stud and the top of the insulator but then that black spot up there at the top, up here, was not completely filled in this case and in certain other of the terminals that we sectioned.

I didn't bring a photograph of the section of the terminal from the 50 ampere hour cell that we sectioned because it looks essentially the same except that we could not see any cracks nor could we see any other obvious form of degredation or damage, at least by normal microscopic examination.

So at this moment I am not certain exactly where the leak path was in that other terminal and in many of the other terminals that are leaking at this time.

I want to make one comment, though, with regard to this and that is that we did determine that in every case the leakage was occurring between or at that point in the joint between the ceramic insulator and the braze compound, and at no other places was there any leakage.

Now I want to mention this because Bob Steinhauer mentioned the business of corrosion of certain braze alloys at metal-to-metal junctions and there of course is concern for the over-all soluability or corrosion characteristics, as you wish, of the braze alloy. But I think in perspective if you look at all of the available data on leakage, I think you'll find that leakage at this type of a terminal or even smaller terminals, that a very large proportion of the leakage

eb6

occurs at the ceramic-to-metal bond and nowhere else.

So I'm not sure in terms of priorities whether we should not be concentrating more on the specific mechanism of formation of leak paths between the ceramic and the braze and relegate some of these other potential leakage problems to a lower priority, because I believe that 99 out of 100, if not more of our leakers are occuring because of some particular problem of formation of that bond between the ceramic and the metal, and not because of any inherent soluability characteristics of the braze alloy alone.

It has something to do with the association of the braze alloy with the ceramic.

(Slide off.)

Now as a result of this particular experience with this particular type and manufacture of seal, we went into high gear on trying to evaluate possible substitutes for a terminal for our existing program. We were aware, had been aware for a couple of years, of the work that GE was doing in developing their own seal and so at that point we tried to gather all of the available information on what testing had been done on the GE seal.

In addition,we-- I'm not going to summarize that because I believe that the people from GE are probably going to talk to you about that but in addition to what had been done, we did some of our own in-house testing of the GE seal

eb7

in comparison to the Ceramaseal terminal that we had been using previously.

We did several kinds of tests. We did what we call the push-to-failure test by stressing the terminals along both directions between the stud and the outside of the terminal to see what the failure characteristics were. We did what we call the stress cycle testing in which we cycled at a low rate at below the yield point and then took a look at the results of that kind of testing.

We did some heat cycling, not quite what is normally called a heat-temperature-shock test, but it involved placing the terminals in an oven preheated to 300 degrees F. for an hour and taking them out and letting them sit at room temperature to cool off, and repeating this cycle many times, and then we followed that by leak testing and metallurgical examination.

We tried some torque testing but the results weren't too successful there, namely because we couldn't seem to find a way to grab onto the stud in these terminals in such a way that the joint between the lever arm and the stud wouldn't give way before the terminal would fail.

But anyhow, we managed to establish at least that from a torque standpoint that all these terminals are at least strong enough so that the weld that we made between our handle and the terminals failed first.

eb8

Then we did one other kind of test on one terminal. The test we did was to fill one of the Ceramaseal-type terminals with epoxy resin of the type similar to that used by the manufacturer of the cell, then to heat cycle the stud with respect to the outside; that is, we put a differential heat cycle, differential temperature cycle, in which the stud was cycled through a large temperature variation while the outside was left with a small temperature variation, and tried to see whether that would induce any kind of visible damage or leakage.

The reason we did that was because one of the mechanisms or determinants or what-have-you that was proposed for the gross failure of that seal on the 100 ampere hour cell that I showed you was that in the process of filling the inside of these terminals with epoxy resin, if then the conditions might have been just right, by thermally cycling this thing, the theory was that because of the presence of the epoxy, there would be sufficient stress applied to the ceramic to cause it to, because of the epoxy stressing the ceramic, to cause it to crack the outside. So we briefly wanted to check on this.

We tested four different kinds of specimens. One was a complete terminal, including the ceramic and the stud as made by Ceramaseal. Another was we happend to have available to us, and we were in a hurry to get some results at the

eb9

time, we happened to have available some of the outside portions of the Ceramaseal terminal without the stud, so we subjected those to certain kinds of stress tests.

Then we had available to us two different sizes of the GE-designed butt seal. One was the smallest one I know they are making these days for cells, which was originally designed I guess for a 6 ampere hour sized cell, and then a slightly larger one intended for use up to a 20 ampere hour cell.

The former is about 7/16ths of an inch in diameter; the latter is about 5/8ths inch in diameter.

Without going into a great deal of detail I would just like to say that in general, all of the-- Well, let's see. We had four each of the medium-sized GE-designed seals. We had six each of the small-sized GE seals. We had four of the outside part of the Ceramaseal terminals and we had six of the complete Ceramaseal seals. So that was our sample.

Some of these were subjected to various tests and others, others, so we don't really have a very large statistical coverage here, but I thought you might be interested in the general results we did get.

What we saw on the pull tests is that for the Ceramaseal type that in each direction, in either direction the seals failed by a parting of the lower ceramic-to-metal bond, and that was the only mode of failure that we saw on

eb10

the Ceramaseal design. This occurred at a force of something between 1100 and 1500 pounds for that sized terminal. It occurred at approximately the same force going in either direction; that is, in what is sometimes called the plus-Z direction, which is going toward the top of the cell in its normal orientation, and then the minus-Z direction is 180 degrees off of that.

In the GE butt seal, we could not get any failures of the bond itself when the seal was pushed in such a way that the force was applied downward in the normal configuration. That is what I call the minus-Z direction; that is, if you set the terminal on a fixture with the normal terminal pointing up and you push down on it, we did not get a failure of any of the ceramic-to-metal bonds until either the metal of the post collapsed or the supporting base structure collapsed, and that occurred at pressures -- at a force of something like five to six hundred pounds for both sizes of small terminals that we tested.

When we applied the force in the opposite direction, that is, we held the outside and pushed upward on the bottom end of the stud, we got failure at the same point, the same bond, in all the specimens, namely,-- Well, I think I am going to have to refer to some figures here:

It was at the lower bond of the upper flange. Let me show you some photographs.

eb11

There are a couple more introductory ones here.

(Slide 60.)

Here is a photograph of the outside only portion of the Ceramaseal terminal. We used these primarily, as I said, because we had extra ones available and we could do push tests because we felt that we were primarily testing the lower ceramic-to-metal bond anyhow.

(Slide 61.)

Here is a photograph of the outside of the smaller of the two sizes of the GE butt seal that we tested.

(Slide 62.)

Here is one that really looks just the same but this just happens to be the medium-sized. You see the structure is identical.

(Slide 63.)

Everybody else is showing cross-sections of this terminal, so here's ours. And the point that I was making is that--

When we pushed downward with respect to this part of the base, the only thing that happened was that this metal structure here eventually collapsed and we stopped testing because we figured that we weren't getting anywhere.

Then when we started pushing upward, the failures

Figure 57

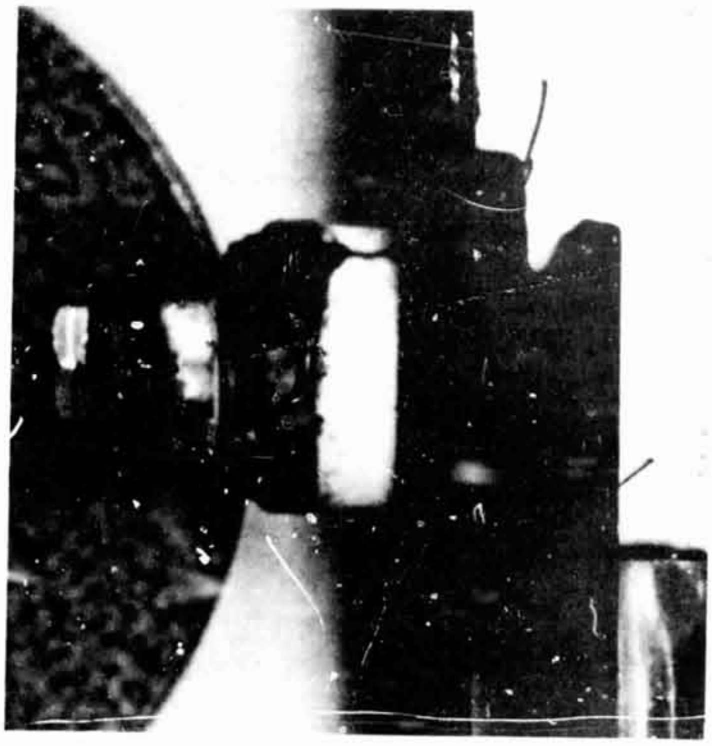


Figure 58

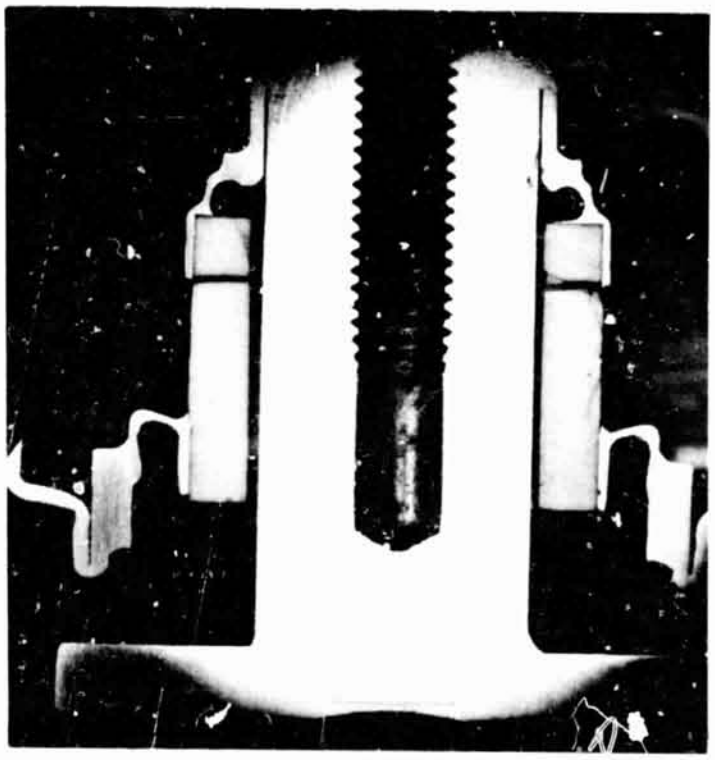


Figure 59

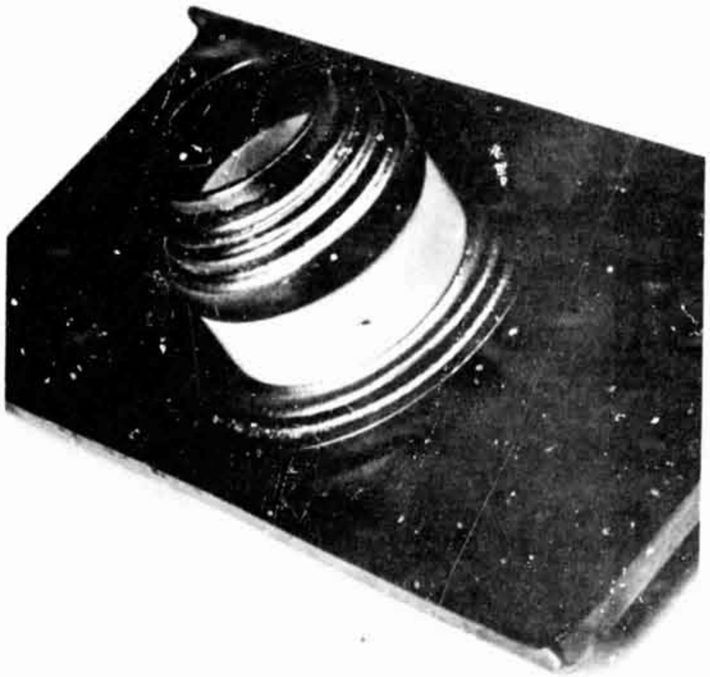


Figure 60

Figure 61

Figure 62

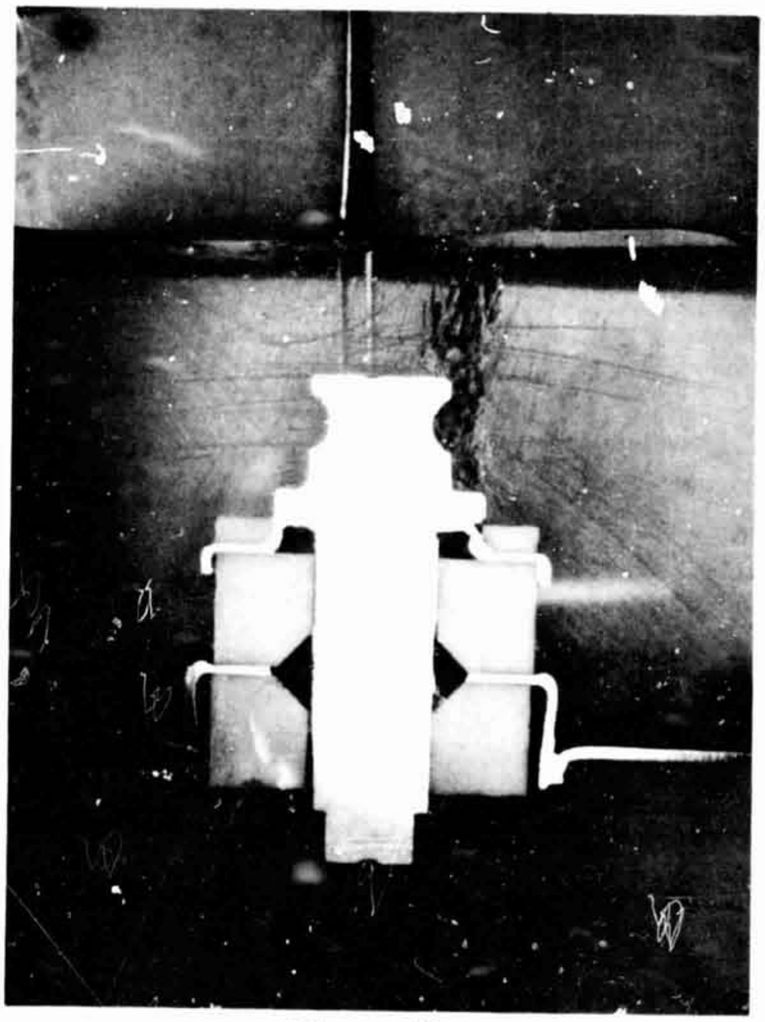


Figure 63

eb12

on all of the samples that we tested were at this lower bond between this flange and this ceramic member here (indicating), and the failures were all very similar.

I don't know whether I'd call it a clean break or not, but the break occurred in the ceramic in every case, and there was a thin layer of ceramic adhering to the flange in every case, and it was a fairly uniform fracture all the way around. Those breaks occurred at about the same force for each of these two sized terminals, which was at approximately 400 pounds of force applied.

Actually, the bond area in these two sizes of terminals is about the same. The bond area in the larger terminal is slightly larger, I guess, but they are similar in bond area.

After the heat cycling that we put samples of all of these through,-- Well, first of all, we leak tested with a sensitivity of approximately 10^{-10} cc's of helium per second on all these specimens before any of these tests were done and we satisfied ourselves that there was no measurable leakage to that level of sensitivity for all these samples when they started.

Then after the non-destructive tests we retested with helium leak testers at the same level and in no cases with the testing that we did did we see any increase in the leak rate due to the test environments that we had used.

eb13

This includes the heat cycling, the stress cycling, and the cycling of the post with respect to the outside of the terminal assembly that we ran on one terminal.

Our conclusion, tentative though it must be, was that as far as those kind of tests were concerned, the GE butt seal design, in terms of inherent strength, was entirely comparable to the Ceramaseal design and as a result, we decided to switch part of our present test and development program over to cells having seals -- having this type of design and geometry.

Our present effort consists of developing a size of the GE butt seal intermediate between the medium sized that I showed you here and a half-inch diameter post. As a matter of fact, in order to optimize weight, we are developing a butt seal design with GE that has approximately a .35-inch diameter stud.

Other than that, the rest of the structure is scaled proportionately. We do not have any of these as yet in hand. We expect to have the first deliveries in January and then we're going to repeat these same kinds of tests on samples of those things, and then we will have a group of cells that we will put under test.

HENNINGAN: Thank you, Dr. Scott. Do we have any questions for Dr. Scott?

One question there.

eb14

MIKKELSON: Mikkelson, Convair.

More of an observation than a question:

We've had some leakage problems with similar zinc cells also, and you mention you found all of your leakage points at the negative terminal. This is where we found ours, also. We chemically analyzed the fluid and found that to be potassium. And again basically the cause of the failure was a failure of the sealing material to adhere to the terminal.

It's interesting, that point. Leakage is at the negative terminal also.

SCOTT: You say non-adherence of the sealing material?

MIKKELSON: Yes. They're not using a metal-to-ceramic seal. In a silver zinc cell you have a different case material and therefore, a different sealing material.

SCOTT: But you are referring to the bond between the terminal conductor --

MIKKELSON: Yes, I am.

SCOTT: -- and the non-insulating part?

MIKKELSON: That's correct. It's just an observation along that point, the same terminal.

SCOTT: Your remarks remind me to say one other thing and that is that in looking at the two failed terminals, one from 100 ampere hour cell and one from a 50 ampere hour cell that we did look at carefully, we saw that as a whole,

eb15

the epoxy potting material was intact; that is, there was a large mass of potting materials used in those terminals because of their size, and in general, it was all there.

However, there was one difference and that is in the 100 ampere hour cell that blew its stack, the surface of the epoxy material was all cracked but there did not appear to be cracking through the bulk of the potting material and there did not appear to be any apparent paths around the outside of the potting material between the potting material and the surrounding metal.

In the case of the 50 ampere hour cell that was leaking, the potting material appeared to be in perfect condition. There was no trace of any damage at all and appeared to be bonding in all respects, and yet obviously somehow or other, the KOH had penetrated.

MIKKELSON: Well, ours is a 100 ampere hour cell and again, we examined the epoxy-like sealing material and again, no signs of any cracks in the material itself. We thought at first that the material was breaking down, but it wasn't.

SCOTT: I cannot say positively that there could not be some kind of a film path between the potting material that we were looking at and the metal that could have led to the leakage. We have not analyzed it that carefully.

HENNIGAN: One question to follow that. Was this

eb16

potted on plastic, the cover?

SCOTT: Yes, it's a Bakelite seal type material and you've got your stud coming up through the Bakelite and you have to seal the stud to the case and you use an epoxy-type material. I won't mention it because I don't know whether I can or not.

But to answer your question, yes.

HENNIGAN: One of the problems we've had with that one years ago is it's difficult to get a good seal there unless you move the mold release that whoever made the part has put on there to get it out of the mold. And that's done by sandblasting all seal surfaces before you have put the cell together. So this might help you out.

Mr. Font?

FONT: Thank you.

Font, from SAFT.

With respect to the leakage at the negative terminal, we have also observed this phenomenon. We have to consider that the electrocapillarity of potassium hydroxide is maximum at the potential of the negative electrode.

HENNIGAN: One more question?

Earl Carr?

CARR: I don't have a question, but I have a

C.3

eb17

statement on the same thing. This is in regard to some ABS cell case, nickel cadmium vented type cells, and again, we see the leakage on the negative terminal when there is leakage.

We had an interesting test going with some cells for Fort Monmouth in that if you've worked with them, they have a test series for 16 cells where the cells are divided and subdivided so that you can trace any one cell through some mixture of environments.

In just kind of an off-hand thing, after we had done the tests we noticed we had a few leaker negative terminals and we went back to see what of the environments, if any, correlated with the cells that were leaking, and we found that the leakage was associated with the 30-day charge retension test.

HENNIGAN: I think it is interesting that presently there are a number of specialized test methods, the so-called double ammeter method that Bob Steinhauer mentioned earlier being one of them, that are primarily directed toward measurement of corrosion of braze materials and so forth at the positive electrode and are not really oriented toward the negative at all. In fact, they really wouldn't function in the same way at the potential of the negative electrode.

And yet here we are talking about most of the leakage being at the negative. I just suggest that we might take another look and make sure that we're not barking up the

eb18

wrong tree.

HENNIGAN: Harvey Seiger?

SEIGER: Several years ago there was a migration problem of silver at the positive electrodes and that was most certainly due to corrosion. That material had been a potential of the positive and those are the conditions for the oxidation and there was migration.

There were two steps taken by two different groups to overcome that problem, and what you're talking about now is real progress. You have left the problem that was extant at that time at the positive electrode and now you have a different one at the negative.

(Laughter.)

HENNIGAN: We'd like to move along here. We have one more paper on the seals, and particularly the General Electric seal which will be given by Pete Voyentzie of the General Electric.

xzxzx

VOYENTZIE: On the General Electric seal, we started development or evaluation back in 1967. The main purpose was to develop a longer life seal having at least an objective of about ten years and incidentally, to have a backup seal.

We decided that in order to obtain a longer life seal right then and there, back in 1967, it would be essential to remove any copper associated with the seal or braze, eb19 cobalt and silver. So the braze that we settled on is a nickel titanium alloy between the ceramic and a nickel cover.

The prototype evaluation consisted of testing of individual components, primarily the choice of ceramic and the new nickel titanium braze for corrosion propertics and in the case of ceramic, tensile strength and thickness loss, and so on, and later on, an evaluation of the completed assembly.

(Slide 64.)

I brought one of these along just in case you hadn't seen it.

(Laughter.)

(Slide 65.)

The prototype evaluation on the component, the ceramic. We obtained large area wafer sections of about one and a half square inches. The temperature of the KOH was 110 degrees Centigrade for one month under reflux, reflux apparatus actually at that temperature; there's no active refluxing, a little bit, not much. After a month, the indicated weight loss and the thickness loss.

The ceramic-- Several types were evaluated including 99 percent alumina. This here happens to be a 96 percent alumina.

At that time back in 1967 it was our intention to use 99 percent alumina to go hand-in-hand with the long-life objectives but the high alumina that was available at that

eb20

time was quite fragile and would not pass mechanical stresses.

Now the other component was primarily a seal corrosion of the nickel titanium braze and the adjacent metal which was nickel, pure nickel. The seal-- In the case of the twin ceramic,the cover was cut in half. One ceramic was made anodic with respe to its cover. The braze was made anodic with respect to the cover and in another beaker on the hotplate.

The other nickel titanium braze was made cathodic with respect to its cover.

We continued this for one month, day and right, and then made sections and what we were looking for was any deposited material that may cause slight shorts, any loss of brazed material, any attack and so on. And in the case of the nickel titanium braze itself, it was as stable as the nickel cover was under those conditions, either anodically or cathodically.

There was no visible attack up to very high magnifications. The helium leak check after this test was completely negative.

Now going to the complete assembly, the actual seal, a torque in the clockwise or counterclockwise rotation of the terminal at the top of the cell took 20 pounds before we could wreck the seal in any way by forcing it clockwise.

Pull tests in the direction that Dr. Scott indicated,

eb21

like pressure from within the cell,-- What we did is we would pull on the terminal from the top -- took a force up to 176 pounds.

(Slide 66.)

After that we concerned ourselves with thermal stresses. We took the seal as received and well, it has to be soldered so we applied a 300 watt soldering iron-- It says 30 up there. And the thermal shock for three cycles at that time, 30 minutes at minus 30 degrees Centigrade, and so on, and 30 minutes at plus 60, a plunge from one temperature to the other within 30 seconds.

Now this was all in the sequence you see it before we went on to recheck for leakage. Had we gotten a leak at any stage of the game we would have stopped at one or two, and investigated further. Fortunately, it didn't happen to be necessary.

After that we took combs and heliarced them to the bottom of the terminal of the seals and then heliarced the cover to the seal case.

And going on now into the pressure tests, we just went right on. We pressured cycled from 150 psig to 38 inches of vacuum mercury. The maximum deformation of the cover under those conditions was 7-1/2 mils.

Well, these happened to be regular cells that we were making in evaluating the assembly so we went into, oh,

eb22

the regular program of aerospace tests including overcharge tests from zero to plus 40 degrees Centigrade.

(Slide 67.)

Taking those same cells after they went through acceptance, we took them to vibration and what we did back in 1967 was to scan the literature and apply the highest vibration levels that we found at that time.

We can put that chart back up a little later if anybody wants to look at it a little longer.

(Slide 68.)

Acceleration and shock at the levels indicated. Acceleration 50 G's, shock 15 G's. After all this, the seals were removed from the cells. We washed the seals very thoroughly. We dried the seals under vacuum and then re-leak checked under helium aspect and found no leaks.

That is what was done, oh, in '67, '68, and NASA-Goddard procured some 45, 50 cells, something in that area, and put them on tests at Crane, Indiana.

So life testing has been done by and large, and we've been relying on it being done by and large by NASA-Goddard at Crane. Our feeling there was that we could test the seals further ourselves from now to doomsday but unless someone else actually did, it wouldn't do us too much good so we were fortunate to have someone else do the testing and carry it from there.

GE NICKEL BRAZE SEAL

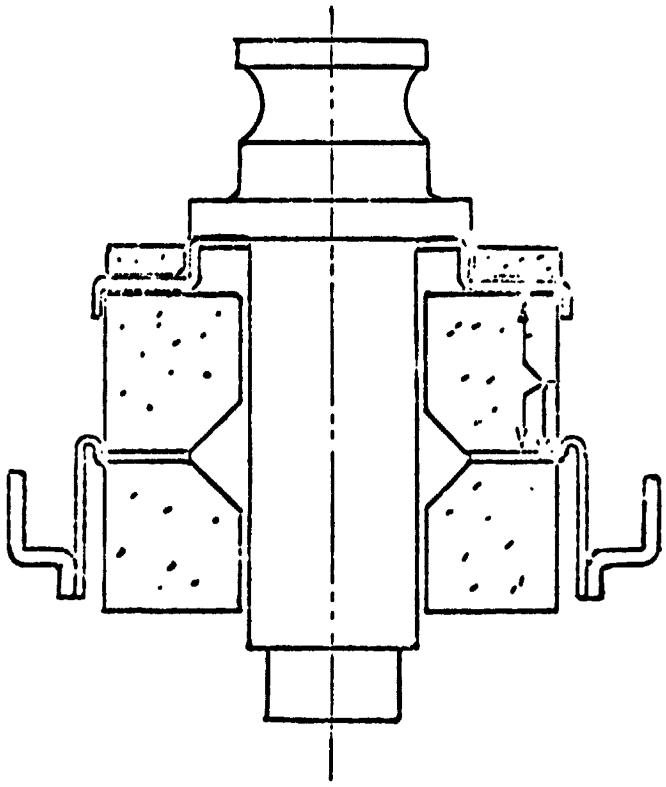


Figure 64

GE NICKEL BRAZE SEAL

PROTOTYPE QUALIFICATION TESTS

CERAMIC Large area wafer sections - heated in [illegible] KOH - 110°C for [illegible] month

Results Weight loss [illegible]

Thickness loss 0.25%

SEAL CORROSION 31% KOH 110°C 1 month 300 MA current. Braze anodic and cathodic with respect to cover. Sections examined for deposits, loss of material, leak checks

MECHANICAL STRESS Torque 20" lbs

Pull tests good to 176 lbs

Figure 65

GO-NO-GO THERMAL TEST

1. Solder. Apply 30 watt solder iron on terminals for 2 minutes.
2. Thermo shock for 3 cycles with 30 minutes at -30°C, then within 30 seconds, 30 minutes at +60°C.
3. Heli Arc combs to seals.
4. Heli Arc cover to cell case.

PRESSURE TEST

1. Pressure cycle from 150 psig to 30" Hg (maximum deformation was .0075").
2. Overcharge test from 0°C - 40°C.

Figure 66

ACCELERATION TEST Accelerate 50 g's for a period of 5 minutes in each direction of the three mutually perpendicular axes.

SHOCK TEST Two 15 g, 5 msec sawtooth shock pulses in each direction of the three mutually perpendicular axes. Total - 6 shocks.

Figure 67

eb23

Since these tests, we have actually exposed the seals to greater thermal shock from minus 60 to plus 250 degrees C. without failure.

Thank you.

HENNIGAN: Any questions? Steve Gaston?

GASTON: Gaston, Grumman.

I missed the size of the cells. Were they 6 ampere hour cells?

VOYENTZIE: Yes, sir, 6 amp hours.

That was the first seal available.

GASTON: Can you also make that seal in a larger size, like for 100 amp hour?

VOYENTZIE: Yes, sir. The seal, since that time, has been made in 6 up to 30-some amp hour cell which is really a 20 amp hour size, and we have made some 50's at the moment, and the 100 amp hour size would use the same as the 50 amp hour size.

GASTON: Did you actually test the larger sized terminal, --

VOYENTZIE: Yes.

GASTON: -- the 50?

VOYENTZIE: Yes, sir. They're on cells and TRW will be receiving some, as Dr. Scott pointed out, and Hughes is getting some very shortly.

HENNIGAN: Do we have any more questions on seals?

eb24

(No response.)

HENNIGAN: I didn't have any more speakers listed for seals. Did I miss anybody?

Oh, Bell Telephone; right?

xzxzx

MC HENRY: Ed McHenry.

HENNIGAN: Sorry about that.

MC. HENRY: This here is a diagram --

(Slide 69.)

-- of the type of seal that we've been working on for a couple of years. Last year I showed this kind of seal. It was originally developed by Ziegler for under-submarine cable.

We have modified it. Last year we didn't have these little rings here and here (indicating) and the old seal-- I now have 4,000 thermal cycles from minus 40 to plus 160 Fahrenheit on the old type. It's gone for a year now, cycling one hour hot and one hour cold with no failures. We had a group of five of them.

So for normal, every-day temperatures it seems this type of seal is perfectly fine.

What we couldn't do is we couldn't steralize them, the old type of seal. They fail, so we developed this with a couple of supporting rings. We have a central terminal. On this particular seal it's a quarter-inch diameter terminal. The outside diameter is half an inch.

VIBRATION - SINUSOIDAL

	Frequency Range, cps	Acceleration g's Peak
Z-Z Longitudinal Axis	5-15	0.06" DA
	15-55	7.0 g's
	55-90	14.0 g's
	90-200	12.0 g's
	200-800	27.0 g's
	800-2000	15.0 g's
X-X Transverse Axis	10-22	0.06" DA
Y-Y Transverse Axis	22-2000	15.0 g's

VIBRATION - RANDOM

The cells were subjected to two minutes of random vibration in each of the three major perpendicular axis over the frequency spectrum of 20-2000 cps. The vibration was performed at an acceleration of 0.65 g^2 cps for a total of 35.9 g's RMS.

Figure 68

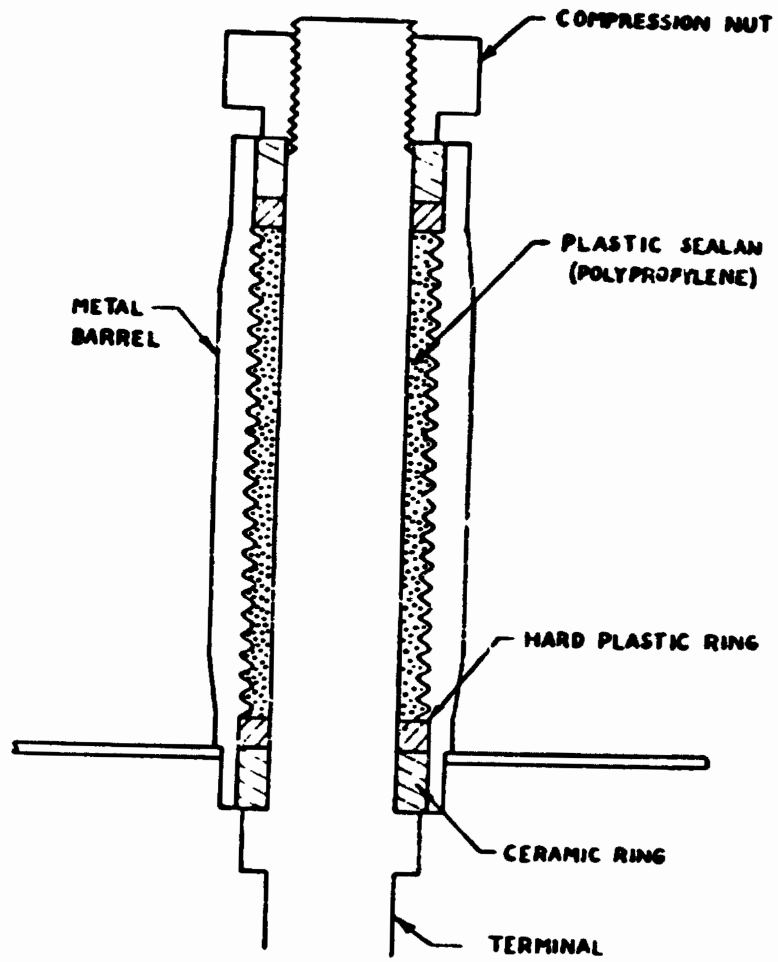


Figure 69

eb25

We have a polyprophylene seal in here. It is injection-molded into the annulus between the post and the barrel. This is a polyprophylene which had a melt flow rate of 3.5 rems per 10 minutes. That is some sort of an ASTM designation on the thing. Presumably the lower the flow rate, the higher temperature it will take before it will melt.

Now here we have-- They say "hard plastic ring." I use teflon. It doesn't have to be teflon but it has to be some higher temperature plastic which will not flow at the higher temperatures.

This was an alumina ring but zirconia would work, or any insulating material which will not be attacked by the alkali would be perfectly fine.

Then we have a nut on top where you compress the rings between the collar on the bottom and the nut on the top. This is to prevent-- On heating as this plastic material wants to expand, the compression rings keep it from getting out.

I made a number of seals of this type using just a ceramic ring with no teflon and I made five of those and put them through sterilization at 135 Centigrade for 72 hours and then I put them on my thermal cycle. The thermal cycle runs from minus 40 Fahrenheit to plus 160 Fahrenheit.

Generally speaking, this type of seal does not corrode. It has no failure mechanism other than an overheating sealant material and having it flow. Or if you cycle it enough

eb26

you will tend to fatigue the thing and it flows a little under heating and then contracts a little and slowly deforms. That is the type of failure you get from this kind of seal. So I put them on thermal cycle as a test.

The ones with just plain ceramic rings, after going through sterilization, two out of the five failed within a few cycles, thermal cycles, within a day or two, and two out of the five have gone through 1500 thermal cycles without failure. So that if done right, if you make a close enough tolerance between the post and the barrel so that this material cannot flow out between the ceramic ring and the barrel, then you don't need the teflon. But the clearances were within a couple of mills. They were supposed to be a 2 mill clearance on the inside and 1 mill on the outside, but in drilling the hole through the center I got more like a 5 mill clearance.

So that these, if they are not properly made, will fail. But when I put the teflon rings in here, teflon will not flow through a small, 4 or 5 mill opening, up until, oh, I suppose about 300 Centigrade or so, so this essentially is just a gasket that prevents this material from flowing by.

This is a force fit. There is no clearance between the teflon and the barrel on the outside or the post on the inside, so that when this material attempts to expand it cannot flow by the teflon and the ceramic simply holds the teflon from flowing out. The teflon will flow through a

eb27

larger diameter.

If you made an all-teflon ring it would all flow out. There's about a 20 mill clearance here. It will flow through that big a hole.

But these seals -- I made five of them this way, put them through the sterilization, 135 Centigrade for 72 hours, and then I've been thermal cycling them now from minus 40 to plus 160 Fahrenheit and they've gone over 500 cycles with no leakage at all.

I detect leakage by using wet pH paper. I feel that's more sensitive than phenolphthalein.

I tried helium leak tests on this but it seemed that a wet terminal does not leak to helium. Even though I know it leaks, if you put helium in the can, it doesn't come out if the terminal is wet. If it's dry it will show up in a leak test, but apparently that does not work well on a wet seal. The phenolphthalein or pH paper is much more sensitive than the helium leak test when you have a seal that's been wet.

And essentially that is all there is to it. It's a very simple seal to make. If you do use the plastic, you know, the teflon backup rings it takes very little talent to put the thing together and although I've only made the five of them, they have gone as far as 500 cycles and they don't seem to leak at all.

The similar, smaller Ziegler seal has shown a year

eb28

of thermal cycling with no leakage and the old type Ziegler seal, we had fifty of those on the Telestar batteries that went nine years without leaking, but they were just sitting there, you know, on storage. They ran through a year or so of low-rate tests.

But it appears this kind of seal is very simple to make. It takes very little talent to put it together and as long as you don't overheat it, they seem to go on forever. That's essentially all there is to it.

HENNIGAN: Steve Gaston has a question.

GASTON: Gaston, Grumman.

What is the largest size terminal you ever tested or even constructed and evaluated?

MC HENRY: It's a quarter-inch diameter post. I never tried anything bigger than that.

I neglected to tell you that this thing is compressed radially. The injection mold plastic is in there and then you compress the barrel and this puts a compressive force on the polypropylene inside.

GASTON: Do you see any problem in going to a larger sized terminal like a half inch diameter?

MC. HENRY: The only problem I can see is that eventually you will get to the point where your outside barrel is so big it will buckle;when you radially compress if you have too thin a wall, instead of getting smaller in

eb29

diameter, it will buckle. I haven't gotten it that size yet.

I think I could put a 5/16ths-inch post in the seal I have now but I'd have to make a bigger barrel. I think for a half-inch post I'd need about a 3/4-inch barrel about an inch tall.

O'ROURKE: Joe O'Rourke, Grumman.

It seems to me like from the picture, one critical aspect of the terminal was how far down you tighten that nut onto the polypropylene. It that torqued to a value or --

MC HENRY: No, you simply tighten it down until you have no clearance. As long as that material is not allowed to flow out-- It has to flow a pretty good distance before-- As long as you tighten it down and you've got no air spaces in there, it's fine.

As the material warms up it gets bigger and the teflon will get bigger, too, and the metal parts don't. They have about one-tenth the thermal transient coefficient, so that the polypropylene really can't get very far unless you've left a large space, but otherwise it's not critical.

HENNIGAN: There's another question back there.

KIPP: Ed Kipp, Gulton Industries.

What sort of a mechanical joint or bond did you have between the barrel and what would be the cover of the cell?

MC HENRY: We used Nioro braze, the real cheap

eb30

stuff. It's a nickel-gold braze alloy, and we've had no troubles with that. We have never tried anything else because essentially-- Well, like aerospace cells, we have put enough money in so you don't fail for some trivial reason. When you fail, you want to fail for a good reason.

(Laughter.)

RUBIN: Rubin, Tyco.

Ed, did you insert the ceramic and hard rubber washer before or after the radial crimping?

MC HENRY: It was all assembled before you crimp it. Let me put the slide back on again.

69

(Slide 69.)

You have a taper here on the top and the bottom. Your crimping tool only extends from here to here and so when you compress it, actually these last couple of threads tend to flare outward a little bit-- Well, they don't flare out; the whole thing is pushed in which gives them the appearance of flaring out.

So there is no compression on the top. You don't compress the ceramic ring at all. The only compression there is when you compress the barrel, the polypropylene wants to go out through the top but it can't because ot those rings, so that would put an axial compression on those rings, but there is no radial compression.

HENNIGAN: Are there any more questions?

eb31

Steve Gaston.

GASTON: Gaston, Grumman.

I have a general question. I wonder if any representative from Ceramaseal is here and has any comments from the findings which were made and which were discussed today and if any solution or comments on that point.

HENNIGAN: There are some people from Ceramaseal. It's up to them if they want to speak.

Mr. Turner? Did you hear the question?

TURNER: I didn't hear the whole question, no.

GASTON: I wonder if Ceramaseal has any comments on the findings which were presented and possibly some of the shortcomings which were pointed out on the Ceramaseal type terminal?

TURNER: Well, I think there are a few things that we can say. Many of you folks may not know how we got into this battery business to start with.

About ten years ago we got involved with GE because we had a seal that seemed resistant to KOH when most of the commonly commercial seals were not. Up until, oh, three years ago, I think about the time the NASA spec was being written, what we were supplying to GE and to Gulton were generally commercial -- so-called commercial seals.

A concerted effort was never made to get zero defects, so to speak, out of what we were building. What we were

eb32

building were modifications of commercial seals, adapted to battery hardware, that is, the stainless steel battery cover and essentially a nickel stud.

As the requirements became more demanding, we made some modifications in our seal system that we felt would make the seal more resistant to the electrolyte. This essentially amounted to some changes in brazing material without changes in the component hardware or the base ceramic material.

Recently there has been a concerted effort by battery users to ask for something that is somewhat more sophisticated than that which we regarded as kind of commercial work. The specifications that we have received from battery suppliers and from battery users have been implemented into our system and we have written specifications as well which have been distributed to battery people which result in much tighter control of material and offer substitutes in component form that are more adaptable to battery work specifically.

Now we have offered in the past to some of our battery customers designs which we have felt were more suitable for battery use; that is, instead of taking what we have adapted from commercial quality seals, we have designed something that we thought would result in lower losses by us, lower losses by our users, and certainly less -- lower leak rate, perhaps even lower than the half to one percent that has been encountered in the sizes up to 20 amp hour in the past.

eb 3

This has almost always been turned down on the premise that there isn't time to fund, although the funds weren't significant, there wasn't time primarily to buy and build and test the seal and introduce it into programs that are currently existing. We have offered these kinds of ideas but they have generally been unacceptable for those reasons until very recently when we made a proposal to Eagle Picher on a 20 amp size, utilizing a design which we think optimizes the similar size that has been used for 20 amp except it incorporates a higher percentage of alumina, hardware that eliminates copper and eliminates some of the other objectionable materials, calls for fit-ups of materials that optimize brazing conditions so that the possibilities of obtaining essentially no losses by the battery user can be obtained.

Now these have not been delivered. We have recoznized one problem recently in what we manufacture, that being the glaze on the outside of the ceramic. This has been used in commercial seals simply to allow easy clearning of the ceramic. It performs no other function. It doesn't make the ceramic gas-tight or eliminate the porosity that people might feel is there.

The recommendation by us on one program to a battery customer, that is, the deletion of glaze, was unaccepted because in the words that we got back: Don't change the design. Don't make it better. Just make it like you made ab34

it before.

The user in this case happens to be NASA, --

(Laughter.)

-- not NASA-Goddard, however; it's NASA-Huntsville.

We think some of the results that Bob Steinhauer has shown in his slides and some that Will Scott gave to us via our battery customers show that the titanium-enriched areas that are referred to by Bob are enhanced by the glaze being in the area.

The glaze as you folks may have seen it in the past is on the area directly adjacent to the braze. However, the glaze penetrates the body, since it is a silica or glass, and it not only penetrates the body in the area in which we want it; it also runs out, so to speak, and down into in many cases the seal area.

We have found this true recently and it was cause for a very serious problem in our plant, and that's the reason we recommended the change in the NASA job.

We think-- It is not only titanium enrichment that Bob refers to but the primary problem there-- Well, he refers to it as time in dwell at temperature. The real problem is that there is glaze in this area and the glaze not only weakens the area but it also allows greater penetration by the titanium into the body; hence that cracking area or that darkened area which results in cracks.

eb35

Now we've seen it in lots of commercial seals over the years. It's not an uncommon thing. In commercial seals it is not something we regard as unacceptable. It's something that we live with because customers want glaze. They like to be able to clean it easily.

The 50-amp and 100-amp size that were shown by Bob and referred to by Dr. Scott, we supplied those to three primary battery suppliers that were referred to and there was not an effort made on those parts to optimize conditions for battery use. That is, we used materials that were essentially designed for commercial applications -- in this case the large size was transistor applications, or rectifier application -- and simply modified those materials to fit them to practical battery sizes.

This was done because of cost, certainly a considera-tion though it is sometimes referred to as not a consideration, and probably primarily time.

We have since examined the materials more closely and in keeping with the current specifications that are now available, all of these things have been tightened up; that is, the controls on all of the components that go into these battery seals have been made such that the variables are going to be minimized and perhaps eliminated, so that the consistency from unit to unit will be optimized.

The units that were shown by Bob Steinhauer's slide

eb36

look to us from the pictures we had seen previously to this meeting, those that had materials on the outside of their tolerance range which gave us probably the worst condition that could exist-- For example, it may not have been evident there but the braze material on those lower collars was probably as thick as the hardware itself, which was a very unacceptable condition.

It's acceptable for commercial work but it's probably not acceptable for battery work where we don't want the starting of a crack so that we don't get KOH creeping in or we don't want it because we don't want to live with cracks propagating after thermal cycling conditions or such.

We think that we have redesigned these things in such a fashion that they are going to be better units. I think the units that I referred to earlier as going to Eagle Picher on the 20-amp size will substantiate that. There conditions have been made such that consistency ought to be very close from unit to unit and I think the reliability upon testing will show that improvement will be substantial, even better than the leak rate that has been referred to as one-half percent.

HENNIGAN: Thank you, Mr. Turner.

Dave Baer, a question?

BAER: I've a question for Mr. Turner.

I'd like to know how he feels about putting epoxy

eb37

in the cavity between the ceramic and the post.

TURNER: Well, that hasn't been our idea. We have been aware that some battery suppliers use this. Dr. Scott referred to the problem of breakage as the result perhaps of that condition. We have actually seen that; at least it is our belief that that has occurred on a 6-amp size that we saw years ago.

The epoxy having an expansion about ten times greater than the nickel stud and even a greater amount to that of the ceramic, it exerts an enormous force when it's heated. Whether it protects the bonds or not substantially, I don't know.

Bob referred today to it protecting the bond, the copper that he referred to, and the fact that there was epoxy on it didn't allow the copper to migrate out. We don't know of any tests ourselves that we have run that would indicate that it's good or bad.

HENNIGAN: Earl Carr, a question?

CARR: Earl Carr, Eagle Picher.

I'd like just to say a few things about the seal that Bob just referred to.

We have, as he said, accepted a proposal from them for an advance design but it's not a drastic great leap forward but progress is sometimes made an inch at a time. And we do feel that this is going to be a good thing.

eb38

This work, and my point, and the reason I wanted the microphone was just to say that this is part of the work that we're going on a process variable study -- that's NAS-521159 -- and it's a pretty wide, encompassing program, but this is the work that is being done.

The other work by other people such as Hughes and TRW has shown some problems recently and this is what we have done to improve the technology. So let's say-- You know, maybe some NASA agencies say, "Well, we can't change the design because it's qualified and you can't touch anything," but at least on this NASA program we are incorporating an advance design.

There's another question. Did you have a question?

GANDEL: Gandel, Lockheed. For Mr. Turner.

Did you say the glaze material was a glass, a silica?

TURNER: Yes.

GANDEL: Wouldn't this be susceptible to attack by KOH?

TURNER: Always on the outside. Always on the air side of the cell.

GANDEL: Okay. And if you don't have the glaze then what is the porosity of the unglazed ceramic?

TURNER: It's essentially zero. There is no porosity.

eb39

HENNIGAN: By the way, if anybody would like to take a look at a Ziegler seal we have some on a cell over here. It's the seal that McHenry talked about. It's on a TI, Texas Instruments, cell. Please don't take the cell because they're kind of hard to get these days.

(Laughter.)

HENNIGAN: Gerry has a couple of announcements, then we'll have a coffee break and then we'll start on the cell performance.

HALPERT: We'll take, hopefully, a ten-minute coffee break.

We do have some items that you may be interested in, some items that developed at NASA, a new integrator, a cell-piercer for analysis of gas from both sealed cells and for plastic cells, and a metal case opener, so if you're down in this area and you want to take a look at the items you are welcome to do that.

HENNIGAN: I'd like to thank all of the participants here.

HALPERT: The second cup of coffee is free.

(Laughter.)

(Recess.)

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HALPERT: Gentlemen, we're ready to start the second segment. We're about three hours late but I think we've got quite a bit of interesting information, and I hope we can continue to do so, with a little more participation perhaps.

Two items just before we get started:

If you didn't get one of these entry passes -- it will save you a lot of problems tomorrow -- I'll be glad to give you one, so please, stop me as I walk down the aisle.

The second point is Tom mentioned an address this morning of William Woodward. Can you all see that on the screen? William Woodward, Director, Space Propulsion and Power, Code RP, NASA Headquarters, Room B-568, Washington, D. C.

Tell him about the problems and how Goddard is helping to solve them.

At this point we have some very interesting work to discuss and Floyd Ford, whom many of you know, has been involved quite a bit with cell experience, and specification experience. Floyd knows what's happening and he is going to chair this session.

I'll turn the meeting over to Floyd.

xxxxx

FORD: Good afternoon.

The day I find out anybody that knows what's going on with batteries, I'm going to get out of the field.

eb2

Well, this morning and part of the afternoon we've concentrated our discussion on separators and seals which it takes to make a good, reliable cell. Personally I have an interest in this because this is what it takes to get a flight-quality battery.

But on the other hand, I have an equal interest in how these cells perform day one, one year, five years, and people are talking about seven to ten years today. I'm interested in how I can look at manufacturers' data and make predictions on what these cells will do under many types of applications. In fact, the types of applications is as varied as the manufacturing processes available to us.

In particular, how does a cell perform for each particular application? How can we predict its performance? And how can we, based on understanding the performance of a cell or a battery, how can we design a system accordingly?

There's two philosophies. One is you improve the product to make it do what you want. The second one, being a user over 50 percent of the time, we design a system to be compatible with the product. And this afternoon, that's the area I think we will dwell on, making the system compatible with the battery.

We have four or possibly five planned presentations this afternoon. They deal from pulse charging to prediction methods to flight performance data, and then this session also

eb3

covers experience with specifications.

Since 1968 practically everyone in this room in some way, shape or form has been touched by specifications, process specifications in particular. In 1968 we instituted certain controls and quality assurance points in the process. As such, we have been collecting data. Some data we really didn't know how to use; some data today we don't know how to use.

We are a point in time where we had better stop and look and see what we've done now for three years, what improvements have we made, what improvements can be made in the next three to five years. What does all this data mean to us that we have?

You saw this morning different types of separator tests. How do we corrolate those types of tests into cell performance? We have different types of electrode capacity tests. We have carbonate analysis being done. How do all these fit into the total picture of cell performance?

Those are the ideas I'd like to discuss this afternoon and I hope we can stimulate your thoughts and your contribution in these areas.

To lead off this afternoon's discussion on cell performance and experience with specifications, we have Mr. Bill Boyd of the Utah Research Center, and his topic is pulse charging.

eb4

xzxzx

Mr. Boyd.

BOYD: Gentlemen, I will first apologize for my voice. I spent last week up in Seattle putting a pulse charger on an A-6-A Navy bomber and the entire week was on the wing, it seemed like, taking data and so cn, so I have a cold and I can't talk too well.

May I have the first slide, please?

(Slide 70.)

I might say this presentation was given about four weeks ago in Cleveland at the Electro chemical Society and Gerry Halpert asked if I would just come and give briefly part of the data which may be relative to the techniques that might be used on sealed cells.

I might also say that the work we have done almost entirely is on vented cells, so keep that in consideration, if you will.

I would like first of all to define, to at least Utah Research, what is a pulse charger. We find in industry there are definitions going around and we'd like at least to give you ours if we possibly could.

Now this happens to be the charger aboard the 747 Boeing aircraft. It also is on the 727 and the 737. They call this a pulse charger for only one basic reason. You will note if you will, this happens to be the current discharge caused by the internal APU drawing 871 amps for about ten

eb5

seconds. It then drops to 448 amps, lasting approximately one minute.

Then normally as the airplane takes off the ground, the charger goes on. The voltage rise profile is as you see here. Time, by the way, is going this direction rather than in the normal direction.

The voltage rise of course is very typical of a constant current charger but notice the current mode if you will. The current of the charge begins at 80 amps or 88 amperes. Now this battery is normally a 34 ampere hour battery built by GE. The current then decreases down in about, oh, 15 or 20 minutes, and then as the voltage rise profile attains approximately 27 volts, the charger is turned off and as the voltage now drops down, the charger goes back on and then a pulse mode begins, and every so many seconds a pulse occurs until eight or nine pulses are accomplished.

This is called a forced mode pulse charger.

Now again, we don't call this a pulse charger as we define a pulse.

May I have the next slide, please?

(Slide 71.)

eb6

Comparative tests run on the 747 with the Utah charger using a pulse mode. You will notice again the same kind of discharge profile because that was required. On the voltage rise, a very similar voltage rise, but now if you will note what the current looks like; again almost a pure constant current charge, in this case 52 amps for a 34 ampere hour battery.

Again we control much the same. As the voltage rise occurs we trip out, we decrease the current down to a very low mode, normally about C over 4, C over 5, or something similar; in this case, 7 amps.

In that case of course the voltage rise now maintains a rather large plateau, a high plateau, and tops the battery out very well.

Let's look at the actual pulse if we can.

Next slide, please.

72 (Slide 72.)

This is how the actual current is going into the battery. We're using SCR controls and I'll show you a schematic in just a minute. But these pulses in this case in this particular value here -- and this trace was taken from a 2-1/2 ampere hour cell, a small one we had a picture of -- the peak, you'll notice here, happens to be 43 amps or almost 20 times the average input current.

12.9

The rep rate is is about 6 pulses per second

eb7

in this case because of the low average values.

Notice also this is the zero point when the SCR turns on. It has residual going negative which is always a common thing in the charger.

Next slide, please.

(Slide 73.)

73

This is upside down, but let it go. It's good enough. We can talk about it.

One charger we have made only three copies, one which went to Bob Steinhauer at Hughes and two went to Fort Monmouth. It was an attempt to build a charger that would have complete variable aspects on the average charged currents and the peak current, the average running from zero to 50 amp and the peak going from zero to 500 amps, independently variable; also being able to change the waveform both in width and so on.

In this case, now the peak here is 300 amps and the rep now is approximately 30 cycles per second. This is an average of 50 amps approximately.

Along with the current itself we have these pulse frequencies varying. One critical aspect we feel that a charger ought to have, at least in the vented cell work, is

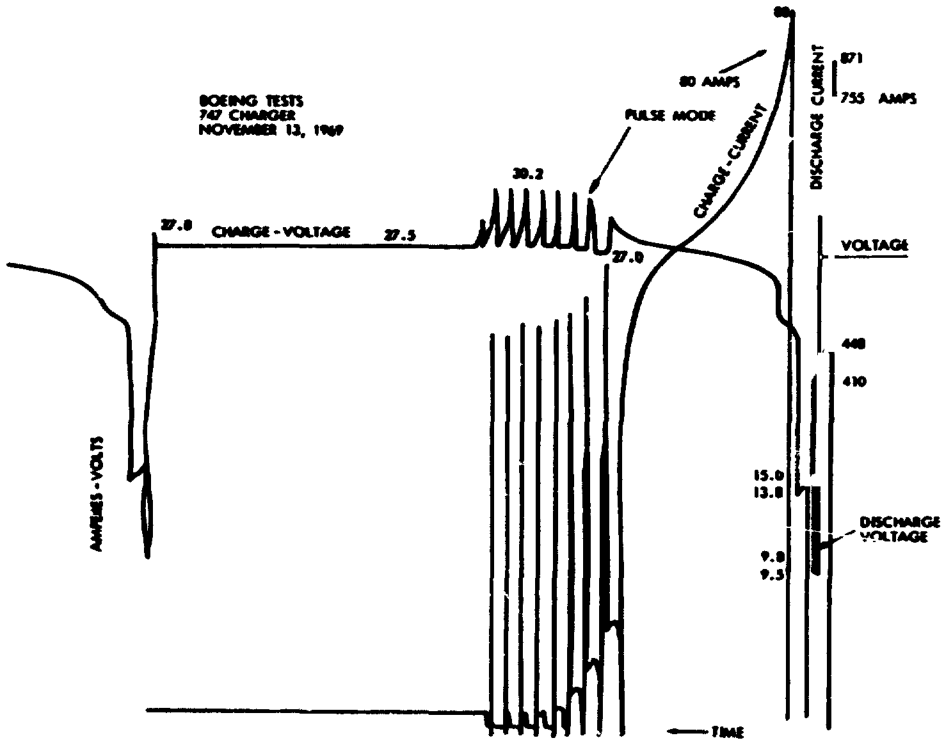


Figure 70

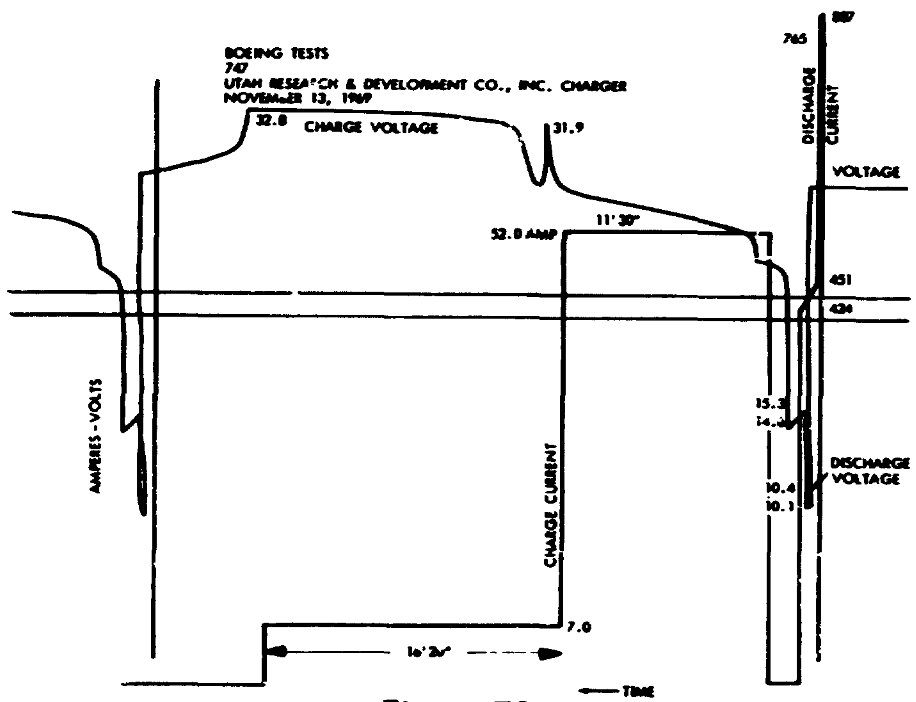


Figure 71

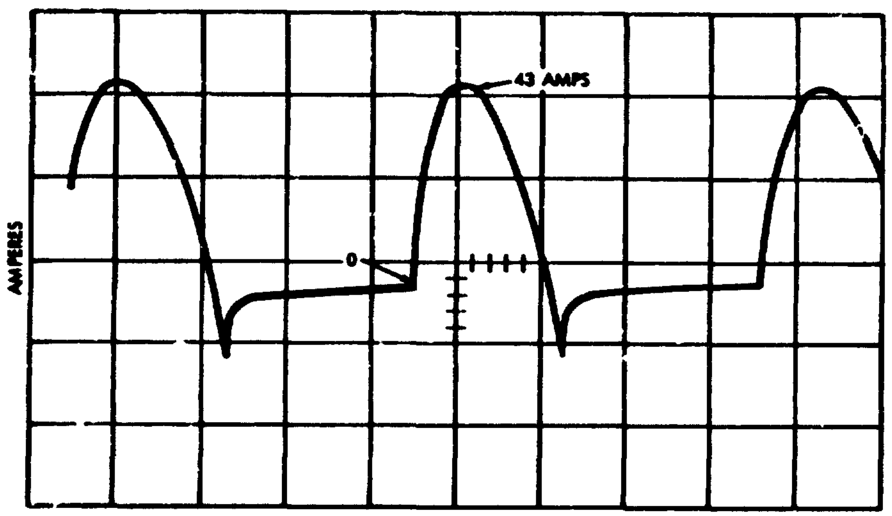


Figure 72

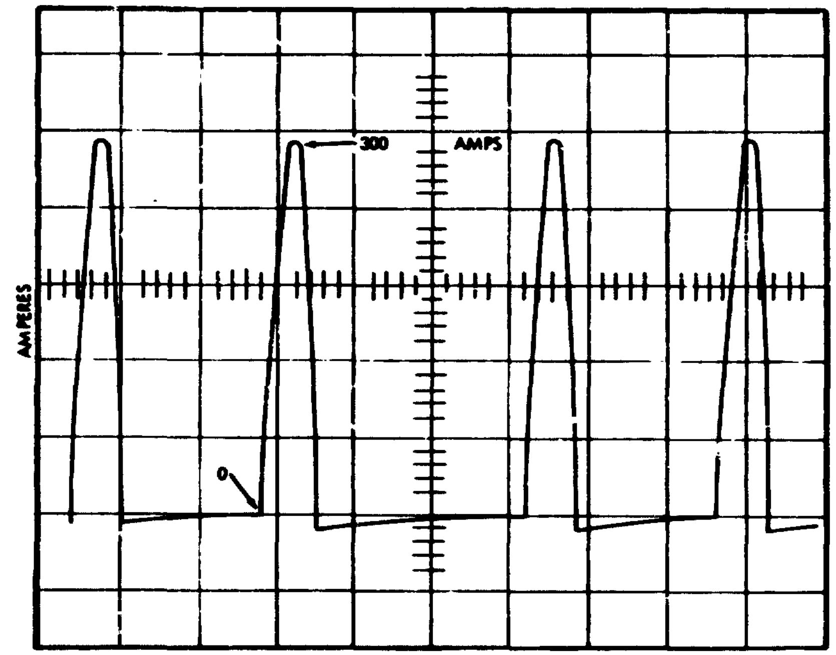


Figure 73

eb8

having the correct charge mode of control. For one thing we know, as this slide will show now, --

(Slide 74.)

-- if you vary the charge rate, of course the charge voltage can vary;going from C over 10 to perhaps 2C, you have almost a complete 2 volts difference on a 19 cell battery, and so if you're going to control off a voltage sensing system, you must change that sensor with the rate of charge as this slide will show.

These data are taken from Boeing, by the way, again people who worked on the 747.

That's fine.

What happened here is a single cell was used to vary the charge rate and they would go from C over 3 to 2C in steps of one minute duration of time as you can see here, and then going up to 2C would cut it back and rest it for a period of time before starting a second sweep.

Notice if you will again the potential variance on a single cell at the various charge rates. I'm sure you are all aware of these curves but again, on the higher plateau, you're spreading almost .2 of a volt for a single cell and almost 4 volts again for 19 cells.

eb9

So I'm really saying that if you're going to charge and control the charge by a voltage sensing system, it should be variable and dependent upon the charge rate.

Next slide, please.

(Slide 75.)

The same thing is true, by the way, of temperature, and very critically so. The majority of problems on the airlines today and of course the military aircraft are based on temperature.

Now Monday I was with the people at Trans World Airlines and you can't imagine the extreme cost that this is costing them because of overheating problems aboard the aircraft.

But here again we have a single cell voltage on my left, and we have here the transfer voltage point. This is the lower region or lower plateau, and of course the upper plateau; increasing temperature to my right, up to 110 degrees Fahrenheit.

You will notice if you will the sloping condition of that curve which I am again sure you are aware of. But again if we're starting an ambient condition at, say, 65 or 70 degrees Fahrenheit and rising to 110, a 19-cell battery will have almost a twofold decrease in voltage so again we say that you ought to control any kind of a charger, pulse or otherwise, based on temperature and vary the potentiality

eb10

charge current based on that value.

So we have this built into our charger, exactly what you see here.

Next slide, please.

More importantly to this group today of course is what really happens to the cells when this pulsing condition is exercised.

(Slide 76.)

These are data taken from the Minuteman silos where the batteries are used to restart the air-bearing gyros, very critically of course in this case because as a Minuteman is torn down and retrofitted or repaired, the first thing that must be done to put it back on the air is to put the air-borne gyro back on the air. Otherwise you have no navigational system.

So in this case they are losing numerous cells. It's about $13,000 a month sometimes, depending on how many are torn down, but the important thing here, these cells were reject cells from the Minuteman silos and would have been thrown away. They were deep cycled and put back for this particular test.

In the constant potential mode, you can see what actually happened.

Now when you start the air-bearing gyro you use

eb11

6-seconds duration pulses of approximately 60 amps and these cells are very small at 2-1/2 ampere hour, and one battery contains 42 cells. And so to pass a desirable value, an acceptance level on these Minuteman silos, the battery has to go ten such cycles to be acceptable.

Again you'll notice the first two failed-- The first three failed and then went beyond and maintained this for approximately 13 cycles. That battery would have passed and gone back on the program with the constant potential mode.

Then this battery failed and came below the value and was immediately put on a pulse charger and again, the peak was 43 amps, the frequency was around six cycles per second. Notice what happened. Now rather than going just the nominal ten required pulse cycles and even up to twenty, which was accomplished with the constant potential charger, these discharge pulses now jump an average of fifty discharge pulses which means two or three times more capacity in these cells.

Four such batteries were tested and the same result occurred every time.

I might just mention that the United States Air Force now are using these chargers in the silos on these cells.

Next slide, please.

(Slide not included.)

One more thing I should show here. This happens

eb12

to be a bank of cha-gers built for the U. S. Army. This bank contains 150 ni-cad chargers. Now these are at Dugway, Utah, where the poison gas tests are accomplished, but the requirement here was to recharge 3,000 ni-cad batteries in a 24-hour period of time with only two people doing the work.

Of course you're not allowed to deep cycle in that condition but you put them back on and they have to be full.

You'll notice right here, if you can see it, there is a spring or a device in contact which is our thermal sensor. We also have one on the bottom of the case so we do control, based on temperature, so we eliminate the possibility of thermal run-away.

This was installed about six years ago, five years ago. The criteria here, written by the Army, was deep cycle the ni-cads every seventh cycle because fading had been occurring. When the system was installed they of course went back to their seventh cycle and they found there was no degradation. The specs were rewritten and changed to the 25th cycle and then as that occurred in several conditions at several times, that also was eliminated.

And now, for the past three to four years, they do not deep cycle. And this is a package of 3,000 ni-cad batteries, a good example of what the pulse is, and I'll show you the pulse mode in just a second.

Next slide, please.

eb13

(Slide 77.)

We have, by the way, several different pulse modes that we use. We happen to have a man who likes to change things rather than always duplicate so every time we get a contract he makes a different kind of a pulser, it seems like.

In this case, in fact, every case we do use SCR control. In some cases, as you see at the top, -- This is being supplied to Westinghouse for deep submergence work, and here again we're going up 443 phase input. In this case they have intentionally wiped out the pulse and it goes in the battery. They have not so far caught fire, the pulser. So we have built the pulser with it. We can take off the filter if we desire to and we hope the data will show that.

This will be delivered in about 10 or 15 days from now.

At the bottom, Item No. 6 which is out of sequence for some reason. This is the NBC-1 battery charger currently built for aircraft carriers by Utah Research. We're supplying some 150 of these to the Navy currently. And again you see the SCR control. The input now is 230 or 115 volt, either way. And once again, they have filtered the pulse though we have intentionally designed it with the pulse internally so we can pull of the filters if they're desirable.

In this case there are some very unique things here It's a constant voltage, constant current, or pulse constant

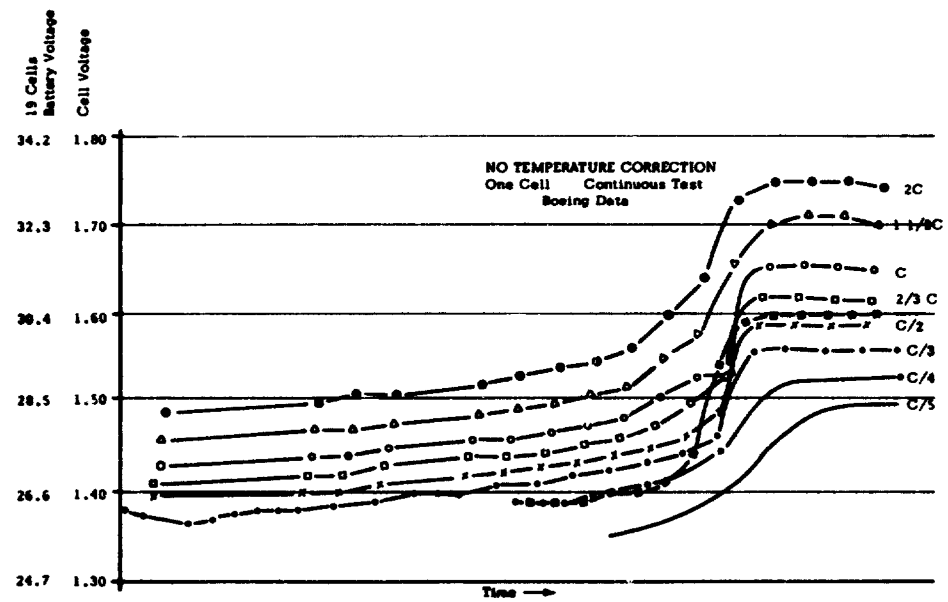


Figure 74

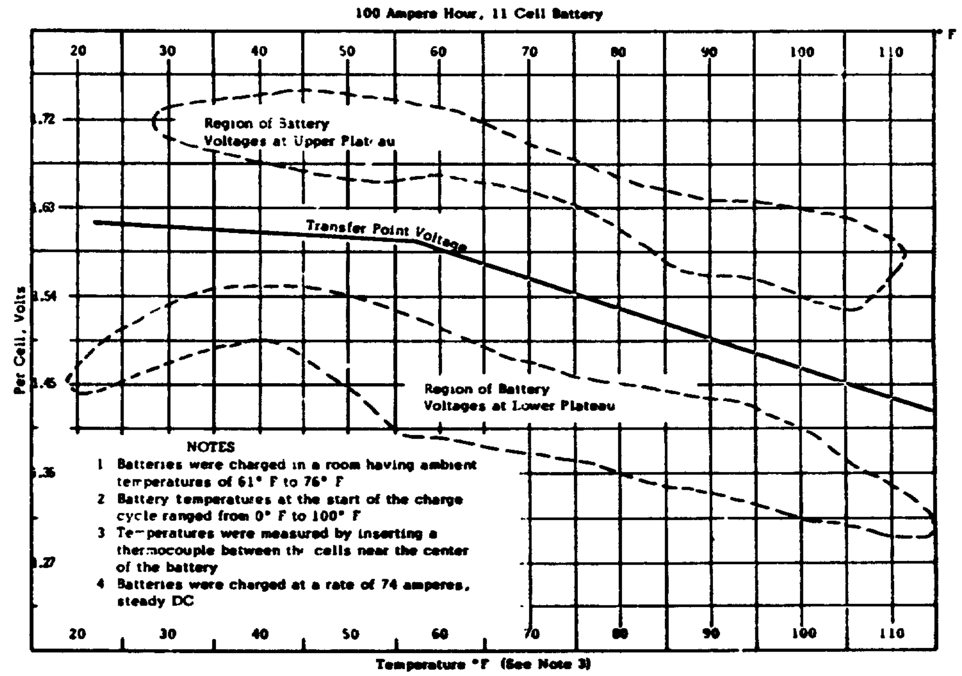


Figure 75

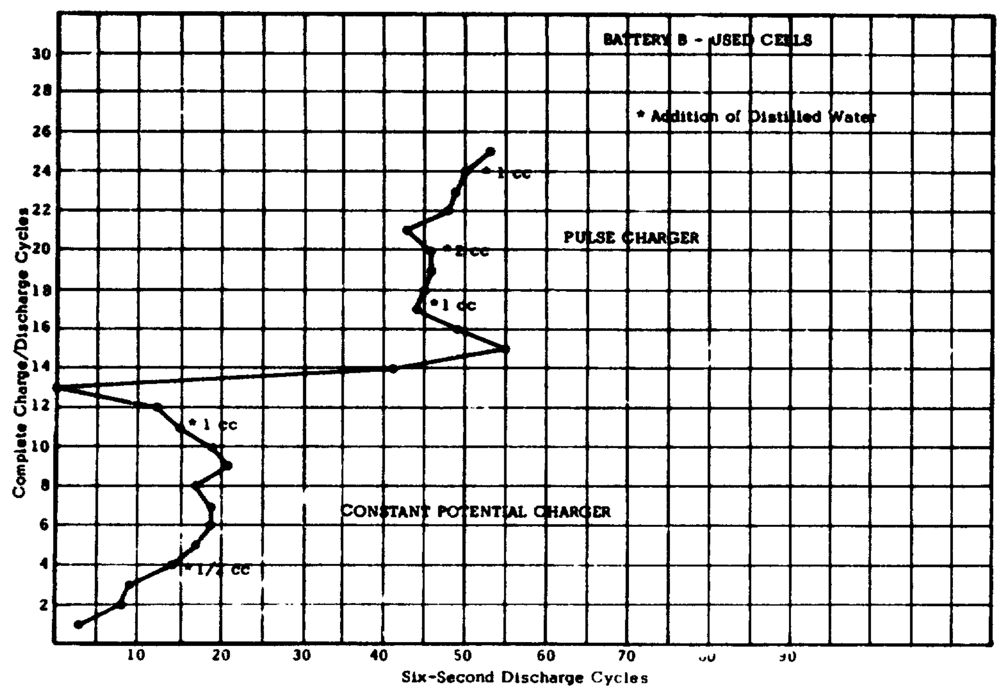


Figure 76

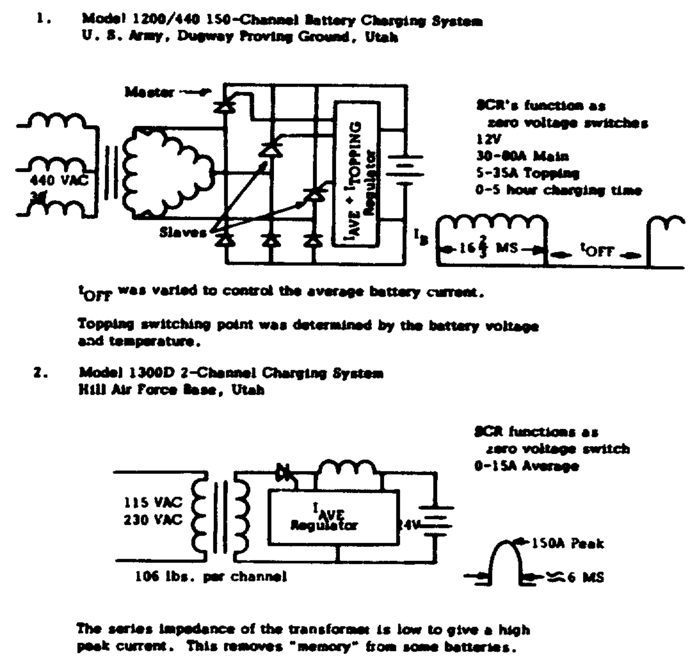


Figure 77

eb14

current charger. It also has a load bank, what we call MJE 3055 power transistors and we actually can control and discharge as well as charge and control the current very precisely.

Next slide, please.

(Slide 78.)

The model 2400 currently is being bought by several airline people, Quantas, Trans World, BOAC, LL, and so on. This is a pulser. It was adapted from the work done at Dugway, U. S. Army.

The pulse here again is SCR-controlled. It's a four-way bridge and there are actually six peaks as the battery is charged every burst. The average current is controlled basically by the time off. You vary the time off, thereby of course changing the frequency, and thereby change the average value.

It goes from zero to 50 amps in the main. It has a variable selection from 10 to 60 percent topping which you can also select. It also have the crossover dependent on the voltage and temperature, which we believe is critical. It also has a case leakage current detector. In case spillage occurs it can turn the charger off.

This is called a fullwave bridge in this case. The other one-- This is the U. S. Army one at Fort Monmouth, New Jersey, and some very interesting things have happened ab15

here.

Now this is not the pulse charger we suggest being used in industry. This is a variable unit whereby you can control and try to define what is a good current, what is a good pulse. So we have the average going from zero to 50, and the peak up to 500 amps. And again, we can vary these independent.

Now the odd thing that happened here when the machine was delivered, the tests were run at high values up to 500 amps and the reports came back, the pulse is no good. You shouldn't use it.

And then they started decreasing the pulse and as the data dropped it came out below 250 or 300 amps, the results were extremely good. And so we are learning by this charger at least that perhaps there are peaks you should not play with; there are conditions you shouldn't go too high on.

And I have a sheet here we'll show as we conclude in just a minute.

Next slide.

(Slide 79.)

I might mention also that Bob Steinhauer has one of these and perhaps he can comment when we conclude here.

But here again we took a 2400 down to Hughes and had rather good results in taking a 20 amp hour cell, running it for two hours at C over 2, and directly cutting it off.

eb16

On discharge two hours later it had about 96 percent output of what was input two hours before. There was no pressure rise and essentially no temperature rise.

Yet when he got this big machine that had the variables he went to the high peak frequency and the high peak current, and even below I believe 40 percent he had gassing and temperature rise occurring. So once again we suggest that we don't go too high on the peak.

This is again the one at Dugway, again the three-phase, 440 volt input. Again it's a full wave. It has the master SCR's and the slaves following. It has again the variable conditions up to 80 amps and topping to 35 amps. This is the machine that has done so very well with the large 80 amp hour battery.

The one at the bottom is a rather different device. This currently is ground support work on the F-4 stations. Again, it's a single wave rather than a double wave machine and perhaps one of the best ever made, by the way.

It has a zero voltage switching of course to eliminate RFI systems so we don't get into generation problems. It has a 150 amp peak continuously; no matter what the value is, it varies the frequency for the average variable and here again, the batteries coming off the F-4 were in conditions up to 50 and 60 percent faded. It took them an average of seven cycles to rebuild these to full capacity batteries and eb17 yet by installing again the pulser on the ground support equipment, they now are full every time.

In fact, rather than 11 ampere hour batteries, the majority are 13 to 14 ampere hour now with the pulsing system. Their manpower has dropped now from 5-1/2 hours maintenance per battery in the shop to less than 1/2 hour and of course we think the pulsing system was the answer there.

Now one more slide? One more.

(Slide 80.)

This perhaps is irrelevant but I asked one of our engineers to draw a schematic of how it might be used on a satellite system where you don't have the frequency and the current inputs or voltage we have of course out here in the shops and so on.

The one on top would be a system whereby the voltage in would be higher than the voltage output. On other words, normally if you had a 24-volt battery you'd have voltage exceeding this some way.

The one on the bottom is where just the opposite occurs, perhaps solar cells, perhaps a 12-volt system where a 24-volt battery is used.

He put SCR's here. Of course that wouldn't be the case. Straight DC input would be required. And all that really happens here, of course, as you get the current flowing through you system with the SCR's turned on, and then you lock into

eb18

a current value, you simply switch off the SCR's, the current must continue flowing through a new path, the diode in the back of the battery.

We believe we could control the pulse form and mode very well in this kind of a system.

That's all the slides, I believe. You can turn them off if you will.

(Slide off.)

Now once again, the data where the peak goes too high.

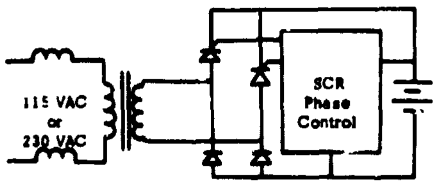
(Slide 81.)

There are perhaps 300 data points available on this as a system now, again where the peak was actually varied to determine whether or not you could get a full capacity battery by various changes. You will note on the peak current, the very first test last year was run at 100 amps peak, the average being 17, the topping 8-1/2.

Notice the battery failed, really. It's a 34 ampere hour battery. The second time, going to 200 amps, we had 34 plus. We don't know how high it would have gone. Merely once it passed it was turned off. The voltage still retained better than about 21-1/2 amps.

This continued on down until we hit the peak of 300. In all three tests you see here, the capacity degraded. Nothing else really basically changed. Even though we had

3. Model 2400A Automatic Battery Charger
Air Lines



4. Model 3000A Variable Pulse Current Charger
U. S. Army, Fort Monmouth, New Jersey

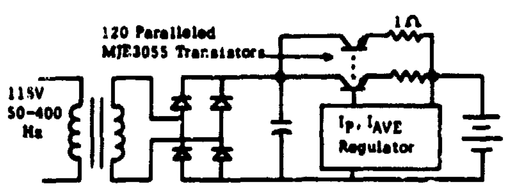
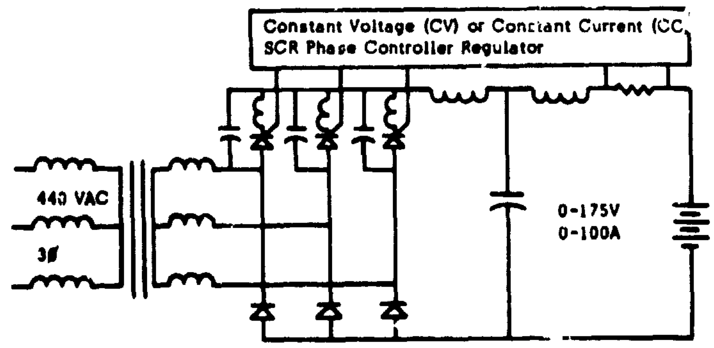
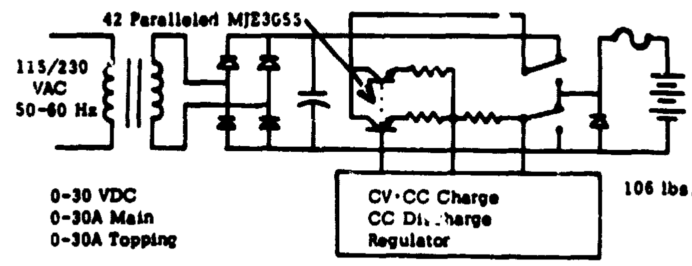


Figure 78

5. Model 175V-100A Silver-Zinc Battery Charger
Westinghouse Electric, Edgewater, Maryland



6. Model NBC-1 Alkaline Battery Charger-Analyzer
Naval Air Engineering Center, Philadelphia, Pennsylvania

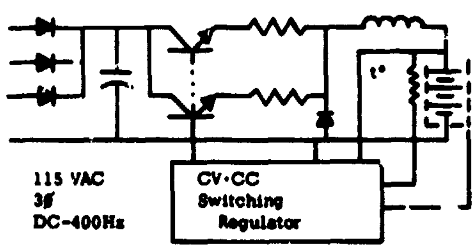


0-30 VDC
0-30A Main
0-30A Topping

Transistor consumes 1000 Watt during discharge

Figure 79

7. $V_{IN} > V_{OUT}$ Switching Regulator



Charge is independent of the input power frequency.
An E cell is used to control topping time.
The cross-over voltage is a function of battery voltage and temperature.
The charger is turned off if the case leakage current exceeds a given level.
This detects excessive cell gassing or broken cells.
Weight - 20 lbs.

8. $V_{IN} < V_{OUT}$ Switching Regulator

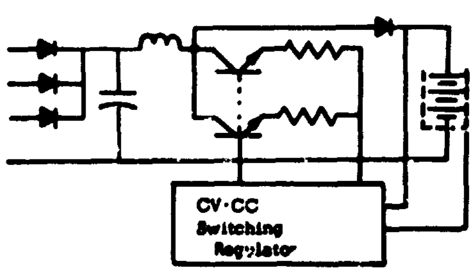


Figure 80

TABLE I

BATTERY CHARGE ACCEPTANCE VS. PEAK CURRENT

URDC MODEL 3000A BATTERY CHARGER
BATTERY BB 433-A-(MA-7) - 34 AH, BATTERY NO. S-2
FORT MONMOUTH, NEW JERSEY

Date	Cycle	Peak Current Amperes	Average Current Main	Average Current Topping	Ampere Hours on Discharge
1/3/70	1	100	17	8.5	27.7
1/7/70	2	200	17	8.5	34 +
1/8/70	3	200	17	9.5	34 +
1/13/70	4	300	30	15	11.3
1/14/70	5	300	25	12	26.0
1/20/70	6	300	17	8.5	29.7
1/21/70	7	200	17	8.5	34.0
2/2/70	8	100	25	12	34 +
2/3/70	9	100	25	12	34 +
2/5/70	10	100	30	12	34 +
2/6/70	11	100	18	9	34 +
2/16/70	12	100	18	9	33.7
2/18/70	13	100	18	9	34.5
2/24/70	14	100	25	10	35.7
3/2/70	15	100	5	10	35.7

Figure 81

eb19

variables in here we had the same inputs we had before.

As we drop down now to 200 or 100 amps, even maintaining the same values here, we're back up to our 34 ampere hour capacity. Now we've seen this many times and we merely are learning now basically if you want to build a voltage charger, keep it normally between -- at least below 250 amps on the peak.

We suspect even further perhaps the frequency is very critical, depending on the plate size and also the wave-form might be a critical aspect also.

Thank you very much.

FORD: Thank you, Bill.

We have a question here. Let me bring the micro-phone to you.

GASTON: Gaston, Grumman.

Do you have any information on the effect of the pulse charging technique on the cycle life, on the total life of the cell? Does it increase it or decrease it, or no effect?

BOYD: The cell life cycle to us-- And a vented cell of course is different than a sealed cell.

GASTON: I'm aware of that.

BOYD: I might read, since you've asked the ques-tion-- Life cycle tests were conducted at Crane this year in July on the battery itself and on the charged cell and they say this:

eb20

"By comparing the results of the life test, the battery charged by the Utah air-borne charger produced higher and more consistent discharge voltage, delivered greater capacity, and decreased the maintenance time required."

They also say:

"The charging time of the Utah air-borne charger was less than the specified time allowed for cost potential charging at 29 volts."

And so the answer is yes, we do have only a few data. We don't have a great deal.

I might mention that the tests at Boeing indicate over a hundred cycles a very slight degradation of voltage, very slight. The capacitor retained its full value.

GASTON: Do you require a special cell design or any standard design can be used for the pulse charger?

BOYD: Oh, yes. We don't touch the cells.

GASTON: You just supply the charger?

BOYD: Right. We do like to have a thermal sensor somewhere in the vicinity of the cells, on the link between the cells or somewhere close by.

One more thought here.

On the charger installed on the A-6-A last week up in Seattle, the batteries coming off the A-6-A are also very much faded. They are normally about 40 percent down and they

eb21

are hard to build back up again.

The first battery on the aircraft which was not removed -- it was just in the condition as it came. When the charge was put on the aircraft, the first charge cycle of two hours, the battery went for two hours and 17 minutes on discharge at C rate. It had, well, 2.4 C actual capacity, an increase of 100 percent of it at least. And of course they're very happy with it.

GASTON: Thank you.

KRAUSE: Krause of JPL.

What effect has this pulse charging on sealed cells and secondly, how would you propose to use this type of charger which requires very high peak currents apparently on satellite systems which have very low current capability usually?

BOYD: I can't answer the question. We have had no data with sealed cells. We've never been offered an opportunity, I suppose. We'd like that chance, but I suspect it is not quite as good as we think it might be.

You hit the point of course also, the low current and the high peak frequency, the high peak value.

Now with Bob we had that problem. By going to the high peak, the gassing does occur. If you keep the peak down low, you might be all right. We don't know that.

KRAUSE: Well, most satellite systems generally

eb22

have low total current output capability. You're talking about a few hundred amps on most of your applications.

BOYD: You're talking of what? 20 ampere hour cells or 50 ampere hour type?

KRAUSE: Say 20 amp hour cells, and the most current you can get out of solar array perhaps is 15 or 20 amps.

BOYD: Oh, well, we could take a low current value and amplify it. That's no problem. Again by the system that Mr. Peterson put on the board, my engineer on this thing, you could take a low current value and use the system to amplify the current peaks. He feels that's at least feasible.

Now how high we could go I don't know. I can't tell you that.

STEINHAUER: Steinhauer, Hughes.

The original purpose for using -- obtaining the Utah charger at Hughes and using it was on the TOW weapons system for a launch battery that stays with the gunner yet uses a 20 cell-- It's a three section battery using 20 cells, 4 ampere hours, sealed cylindrical and two sections with 42 cells of approximately 1, 1.2 ampere hour each.

We were looking for rapid return of the charge, top-off type charging rather than having to dump the residual charge and then return full charge. We ended up, because-- Using the dump type of charge method and returning a four-hour

eb23

charge for four hours in that system-- The Utah work was to make an improvement over that.

We felt not that we would gain in charge efficiency but that we might be able to top-off charge in that case. We have been interested in it. This work was done back in '66 I believe, or '67. We have been interested in it from a space standpoint but we haven't been able to apply it to space cells because of funding limitations, but it has been intriguing to consider it.

It is true that the solar panel capability is low but pulse techniques could be worked out.

What happens in flight morphology under various pulsing regimes and would this indeed give us an enhancement of cycle life and get away from memorization or some of the other effects we don't know, but it's intriguing and I think it is worth exploring.

GROSS: Gross, Boeing.

In answer to Stan Krause's question, Stan, you can get the high current by loading and unloading the A coil.

BETZ: Fred Betz, Fairchild.

I had some limited experience with vented cells and the fading that you have indicated is somewhat typical of constant potential charging --

BOYD: That's true.

BETZ: -- in which the electrodes get imbalanced.

eb24

Once you have a sealed system where essentially you're negative cannot limit the charge, that type of problem is not apparent any longer. We'd have to really look at it from the point of view of cycle life, long-term enhancement or something else. It is not going to recondition a 50 percent battery to 100 percent just like that.

BOYD: I concur. We think the same thing, by the way.

HAINES: Haines, from Defense Research Establishment, Ottawa.

I found your paper quite interesting. Six or seven years ago we in Ottawa built a pulse charger much the same as you have here. In fact, your circuits looked almost identical with ours.

(Laughter.)

BOYD: I haven't seen them.

HAINES: I know you haven't. It was a classified --

BOYD: Thank you.

(Laughter.)

HAINES: -- project at the time, but it was a power supply for a sonar in which we were required to produce approximately 20 pulses every half second with four and a half seconds to reach our capacity.

The battery power supply was 150 volts and I think we were taking the currents out to something like 300 amps.

eb25

We did not use voltage sensing like you did. In Ottawa we're rather afraid to trust ourselves with anything like voltage sensing. We used a coulometer and we found that by using a coulometer and using it pulse technique we could operate ourselves at approximately 1.58 volts, taking advantage of the surface charge for the next pulse discharge.

This allowed us to use considerably less cells with a considerable saving in weight and volume. We were using 65 ampere hour cells.

I might add also that we put something in excess of 100,000 cycles on these cells before they left our establishment and on dissecting one of the cells, we could observe little or no damage to the cell components. By cell components I mean the nylon woven separator and the cellophane.

These were vented cells.

The other thing is-- Let me say one more thing. I believe that the prime reason for using the pulse is mainly in the overcharge so that you can put the overcharge in at a rate where you get a higher efficiency conversion without unduly increasing the temperature of the cells.

Now if you can adequately project the point where you pass over from the point of main charge to the overcharge mode, you can get away with high current direct charging and produce the same effect as you have here. But you have to have a very good indicator of when you're going from main charge to

eb26

overcharge.

BOYD: I might comment on that if I can.

HAINES: Might I add the question I wanted to ask is:

If you are using temperature sensing, how do you derate it if the battery is being used in an engine-start mode, because we have found that to use a battery in an engine-start mode, the temperature of that battery will increase approximately 35 degrees for engine start, as the start occurs.

BOYD: Right. That's right. The charge mode doesn't occur until that is over.

HAINES: No, but if you're using the currents that you have here, you will be into the overcharge mode before that battery has ever had a chance to cool down.

BOYD: Now in this case again we observed the temperature of the battery. We have also a temperature sensor for cutoff. If it gets too high it is derated, both derated and also cut off. It will only go so high, perhaps 120 degrees Fahrenheit or less, before it gets derated in terms of the actual temperature control.

By the way, we do observe the off voltage rather than the on voltage between pulses. It's a much better way of controlling, rather than the actual value rise during the current time.

Second, we do have an E cell in here, the little box

eb27

x

that you saw, the controller. We didn't explain all the details of that box. We do use an E cell which is a coulometer much like you do, also, but we sense the voltage and derate the current, based on the voltage, on the temperature of the battery so that the mode control is based on a decreasing voltage potential with increasing temperature, and the

x

coulometer actually siphons off a part of the charge current and then as you switch from the top -- from the main mode to the topping mode it reverses itself and it controls the energy balance. We call it energy balance. So you get a percentage value of topping which is critical also.

HENNIGAN: Hennigan, Goddard.

As far as pulse charging of sealed cells, a couple of years ago -- oh, it was about '64 -- we had a satellite up about seven months. We started to run short on power and started to pulse the sil-cad battery and destroyed it, and we showed on the ground what happens. We started to overcharge it, and I would expect the same things would happen to sealed silver-zinc cells if you tried to pulse charge sealed cells.

You know, some of our satellites are non-magnetic but it is my understanding that all satellites have to be magnetically clean or else they start to twist as they are crossing through the earth's field. And if we did this pulse charging in the satellite I would expect we might have quite a

eb28

shielding problem, trying to keep the satellite stable.

Thank you.

FORD: One last comment?

HENNIGAN: First, I have copies of the circuits here of all the chargers we're using in case you'd like a copy of them.

Then secondly, if you control the SCR correctly, there is no magnetic RF generation. We've had that problem before. It's very critical so we don't have RF generation, so that's important.

Here again, because of the actual switching condition-- We have some protection if we do have that condition existing but on the air-borne charger, no, it's not there.

FORD: Okay. Thank you, Bill.

While we're on the subject of charging, our next topic is along those lines and is to be presented by Charlie Thomas, Chrysler Corporation's Space Division, and his topic is Evaluation of Improved Charge Methods.

xzxzx

THOMAS: I've been mentally editing this presentation to reduce its length, considering the time of the day, and I may have edited it down to the point where there are some gaps in it. So if I don't adequately explain anything, you can pin me down after the talk.

Chrysler undertook several months ago a program involving development of charging equipment that would provide improved characteristics from cells and evaluation by means of life tests of systems including typical cells in a satellite system utilizing these improved systems.

Now we developed three systems that we are evaluating concurrently in a test program. The test conditions are exactly the same for the three systems with the exception of the charging methods. We've got three groups of cells that are identical, bought at the same time that are being tested in the same room, the same temperature, basically the same depth of discharge, as close as we can get it with the resolution of equipment that we've got, the same 60-30 minute time cycle. The only difference is in the method of charging.

Now let me at the beginning say that the method of charging that we're using is not a pulse charging approach. Now I'm going to be talking in terms of, to describe these charging methods, be talking in terms of peak charge but this is not a transient condition but a steady state charge condition at charge termination.

Now our theory was -- and the same theory I think is supported by many users of batteries -- is that we should try to eliminate overcharge in sealed cells, overcharge of sealed cells on satellite systems to reduce the generation of oxygen pressure, reduce power dissipation, to increase life and also to reduce problems with seals and so forth.

Now Chrysler had been kicking around possibilities for accomplishing this. How can you limit the peak charge level of sealed batteries, sealed cells, to less than the maximum? Now one thing that we were interested in was some means of measuring the state of charge. Unfortunately, nobody ever came up with a way to do that.

We can, with an ampere hour integrator, compute a state of charge value but the accuracy of the computation taking into account the errors of the computer itself and the variables of the cells is not too good.

So what we decided to do was compromise between conventional systems and a system in which the peak charge level would be held to less than 100 percent. We came up with what we called a programmed peak charge or PPC method. Now this method would involve limiting the peak charge of the battery less than 100 percent except for periodic orbits or cycles when the charge would be brought up to as high as you could get it to reset the integrators, in other words, to cancel all of the errors that have accumulated in the state of charge computing circuits.

Now at about the same time we decided to evaluate this method we came up with the idea of possibly using a slightly different approach on auxiliary electrodes for state of charge sensing. The conventional auxiliary electrode basically is an oxygen pressure sensor, or it gives a signal related to oxygen pressure.

eb31

Now we decided to attempt to use what is essentially a recombination electrode which gives a signal related to oxygen pressure at a lower concentration or a lower oxygen pressure, hoping that this would give us a signal, a usable signal at a somewhat lower state of charge.

So we have-- Let me show you the charge-discharge profiles that we're using now. We are evaluating these two --

(Slide 82.)

The top graph shows a typical satellite charge-discharge profile showing the attainment of a hundred percent charge or maximum charge shortly before the end of the cycle, allowing a slight trickle charge period.

Now with the LPC method or the limited peak charge method, as we call it, we would limit the peak charge to less than a hundred percent during each cycle by means of this signal from the recombination electrode. We'll use that as a signal to terminate charge.

With the programmed peak charge method, we keep the peak charge level at leass than a hundred percent except at the periodic orbits when we charge to a hundred percent.

Now actually there are some cell -- slight differferences in cells involved here, too, because by limiting the peak charge to less than a hundred percent, we reduce the oxygen evolution that causes internal pressure buildup and of course ni-cad cells -- sealed ni-cad cells are

C.4

eb32

generally operated starved, which means with probably less electrolytes than we'd like to use from the standpoint of heat transfer and getting goo.. performance characteristics.

The third column indicates this is the significant difference, the most significant difference between the cells, at least I think: In cells that we charge by the conventional method, 19 percent; electrolyte cells that we charge by the PPC method, 21 percent; and cells that we charge by the LPC method, 23 percent.

Now this is not a great difference in percentage but this makes a lot of difference in the rate of recombination of gases and consequently the amount of charge that these cells can take.

Also, we discovered that this makes quite a difference in the way the cells can be charged. Now the top graph shows the charging current profile for the in-between cycles of the PPC method. For this test now we are discharging to a 40 percent depth of discharge. We're charging at a constant rate of .8 C for the in-between orbits when we charge to less than a hundred percent.

Let's see, for subcycle 1 is when we drop from a hundred percent down to -- from a peak of a hundred percent down to a peak of 90 percent on the next orbit.

For subcycles 2 to N, we charge to .8 C for a longer period of time.

eb33

For subcycle N, we have to come back up to a hundred percent. We charge at a higher rate of 1.3 C, dropping down to .4 C and then have a third step which probably is not essential at a rate of C over 12.

Now the best illustration of the benefits of this charging approach and having more electrolyte in the cells is shown here.

(Slide 83.)

This is the comparison of the charging current profiles for the LPC method in which we limit the peak charge to a constant low level during each orbit, and the conventional system where we charge it up as much as we can at the end of each cycle.

Now we did considerable work trying to optimize the charging current profile for the conventional system to enable us to get as much capacity in as we could within the time period that we had available. Now for the tests we're using a typical 60-30 discharge-charge period.

Initially we started out trying to discharge to 50 percent during each cycle, using a 50 percent depth of discharge. It was just not possible with the conventional cells to do that because we just couldn't get out end of discharge voltage up or keep it up without going to too high an end of charge voltage.

So we finally, because of this problem, had to

eb34

reduce our depth of discharge to 40 percent on all three systems.

Now with the LPC method we never overcharge; we charge at a constant rate of .8 C until we're ready to terminate. It is not necessary to use a depth profile.

Here I have some preliminary data. All I have so far is preliminary data.

(Slide 84.)

84

We have something like eight or nine hundred cycles on these cells. Now this shows,again for a satellite-type of orbit, a low-earth-orbit satellite, 40 percent depth of discharge, what we get from the three systems during a complete cycle.

Now notice for the conventional system that during discharge, the end of charge voltage drops down almost to a volt. Also, notice that the charging voltage required for the conventional cells, for the conventional system, is higher. The energy efficiency is quite a lot lower for the conventional cells. You get lower output voltage and it takes a higher voltage to charge. And of course the charging currents, at least during the early part of the charging period, are comparable.

Now another thing that's significant is that with the cells used for the PPC and LPC systems, which have more electrolyte in them, you get a very sharp tailup in the cell

eb35

voltage which, if you are using cell voltage for control, gives you a much better signal to work with.

Now like I say, we have only preliminary data at this point. This last test that we have going now will last for as long as we think is necessary to get precise data which establishes conclusively the lative merits of the three systems. As the data is firmed up, we will make it available to anyone who is interested.

FORD: Thank you, Charlie.

Do we have any questions?

(No response.)

Okay. Thank you.

The trend today, as it has been over the past five or six years is toward larger nickel-cadmium batteries simply because we are requiring more power for each application. Looking down the road to what's ahead in the future, we have many plans for a space station.

In conjunction with that, these programs that have been mentioned this morning to develop large ni-cad cells, 50 ampere hour and 100 ampere hour cells, are in progress. One of these programs that is being funded by NASA, the prime being Grumman Aerospace Corporation, is the development of a 100 ampere hour battery for the space station.

To talk about this program this afternoon we have Steve Gaston, Graumman Aerospace Corporation.

CHARGE CONTROL METHOD	CYCLE NO.	DEPTH OF DISCHARGE (%)	AMBIENT TEMP. (°F)	CHARGE CURRENT PROFILE	CHARGE/ DISCHARGE RATIO	CELL PRESSURE (PSIG)		CELL CASE TEMP. RISE ABOVE AMB. (°F)	
						MAX	MIN	MAX	MIN
CONV.	280	37	65	19/9/2 AMP	1.05	13.5	9	12	7
PPC	242	42	65	24/11 AMP	1.12	44	33.7	15	10
LPC	352	39	65	22 AMP	1.11	56.5	50	13	8

Figure 84

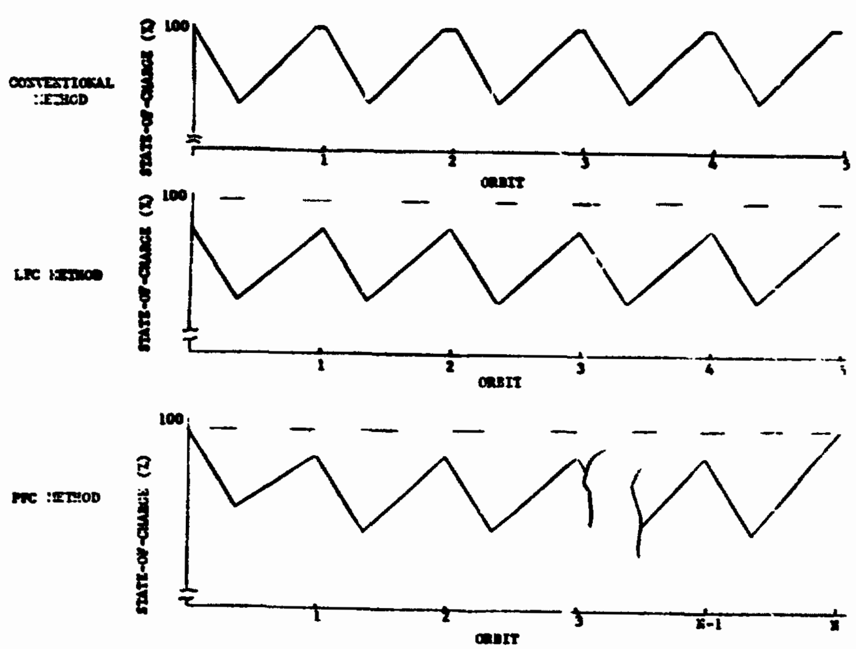


Figure 82

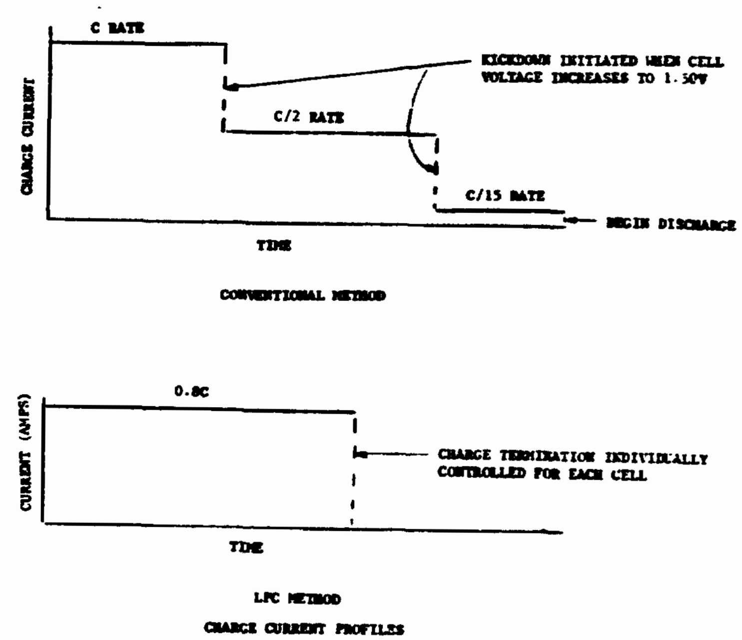


Figure 83

eb26
xzxzx

Steve?

GASTON: The program was funded under contract NAS 911074 and its goal is the development of a 100 amp hour battery. I'd like to just briefly touch upon all the other phases in the program and emphasize the cell-development portion.

The program is by no means complete. It's under-way and we have partial results and more results will come out as we go along.

The major phases in this program are the cell development of the 100 ampere hour cell. There is also a module development and the modulator is used in the space station as a building block. And the space station, according to the latest studies by prime contractors which have just been completed, will look most likely like 672 cells of the 100 ampere hour capacity.

In order to break the battery down to a building block, we like to use the term "module," and from the human factors and reliability and maintainability, we come up with a number of four cells per module.

I put a mockup on the side (indicating). This is the way most likely a module will look like in the space station as we see it now.

In the module development we are working on -- we are constructing two different modules, the first one for

eb27

thermal study which we have completed, and I will show some slides on that later on, and there will be a final development module which will be fully acceptance tested.

In addition, this development of test controllers for these batteries -- or for these cells, I should say, and in addition to that there will be some parametric cycling on cells which would be conducted at Grumman to determine the characteristics that characterize the cells, and there is a life cycle memory-type test program to complete the program.

To emphasize the cells in this program I'd like to show you the first slide.

(Slide 85.)

To start out to make the program cost-effective, we went on a parametric basis. We started out using the OAO cell spec and the NASA interim cell spec, used design inputs to modify some conditions which exist as you go from vendor to vendor to accomplish -- to accommodate the design change variations which are on the cell.

We then came up with a standard design which we also like to call a baseline design and then we broke it down into three different test groups. In Group 1 we test the variation of plate thickness and the terminal configuration. I will go into it in detail a little bit later on. I have an X-ray; I don't have a picture of the terminal

eb28

configuration but I have an X-ray and I think it might serve the purpose.

Then we finalized the terminal configuration and plate thickness and then we went to group 2, where we tested for the separator compression and electrolyte quantity. In group 2,-- Initially we started out with nylon design. In group 2 we introduced polypropylene design. And we have now two polypropylenes..

At the moment we have completed groups 1 and 2 and right now group 3 is being constructed.

In group 3 we introduce two additional polypro-phylenes, different vendors. We still have the nylon design as the standard design. We have an additional input from some auxiliary electrode studies; we weren't too happy with the earlier auxiliary electrode results.

And we still have to finalize the terminal and that's -- the problem of the large terminal seal is very close to my mind. And then we will mechanically test those cells and finalize design and characterize it by the parametric cycle tests and then we go to life cycling tests.

At the same time we have made use already and we will make more use of the NASA process variable study which is under NAS-521159. It investigates certain variables, production variables which we will use as an input in the finalized cell. We already have used some in the group 3 --

eb29

It's not indicated too well, but we have used the plate manufacturing process in group 3.

In addition, we will run some accelerated materials tests which have not been held yet; in particular, some of the terminals have been held up because of some of the recent problems -- possibly long-term seal problems on terminals.

We constructed four thermal simulators for our thermal module. What we have done, we took expanded nickel mesh and interwoven with active plates and now we can use the cell and we did build our engineering module and we have completed thermal tests on that, so we can both use the cells as a heater or we have electrical active cells.

We did conduct some calometric tests, not extensive ones, at the cell vendors, and we will also use the NASA calometric -- the NASA coulometer to get some more extensive calometric information.

We did complete the thermal battery design and all these inputs will then be analyzed and used for the final cell and module design.

I have a picture here of a cell, to give you an idea what our ampere hour cell looks like. If you look at the gauge, it is not the gauge we are using. We're using a compound guage to measure vacuum and pressure. Also, we have a gas inlet and outlet on the side with a valve so we can make adjustments if that becomes necessary.

eb30

This is the baseline design. I have some numbers here, the over-all dimensions. It's about 7.34 inches wide, it's about 1.46 inches thickness or what you call length, and it's about 7.3 inches high. That excludes the terminal; the terminal is about 8 inches high.

We also looked at the opposite or the opposing end terminals and that's somewhat larger. The standard design weighs about 8.8 pounds and the opposing terminal design weighs about 9.5 pounds. We pay a penalty.

(Slide 86.)

It's not a very good picture but I think it gives the idea. One terminal is at the top; the other one is at the bottom.

I also have an X-ray of the heater cell. It shows the two terminals and the two heater terminals.

I would like to summarize the accomplishments which we have done so far.

(Slide 87.)

Besides the variables which we have evaluated -- which we haven't evaluated, or the terminal configuration, the electrode thicknesses - and I will present the electrode results later on -- we evaluated the stack pressure and the number of electrodes. We've done some work on the electrolyte quantity. We've reduced the electrolyte quantity by taking out electrolyte.

We have looked at auxiliary electrode construction and we have looked at the separator which consists of nylon as the standard and polypropylene as the new material.

We looked at the filling technique and in combination with Eagle Picher, the vendor, we have developed a technique which eliminates atmospheric contamination during the filling. It's all done with inert gas in a glove box.

(Slide 88.)

We looked at the seal leak test procedure and we've come up with a new procedure which consists of back-filling with helium while the cell is dry. Several years ago there was some experience by the Relay people where they found that the helium leak test is not a valid one when you have a surface layer of other material, which could be water or electrolyte.

I think it was mentioned before; somebody mentioned it before that if you had a surface with adhesion, the helium leak test will be masked. If you have small pinholes, it will not show because the liquid is there and therefore we feel that once the cell has been filled with electrolyte, the test is rather insensitive, so therefore, we developed this technique of the helium leak test before the cell is filled.

We redesigned the cell terminal studs, and that's both internally and outside, and I will go into it later on. Essentially we wanted to reduce the stresses when the intercell connectors are placed on the cell.

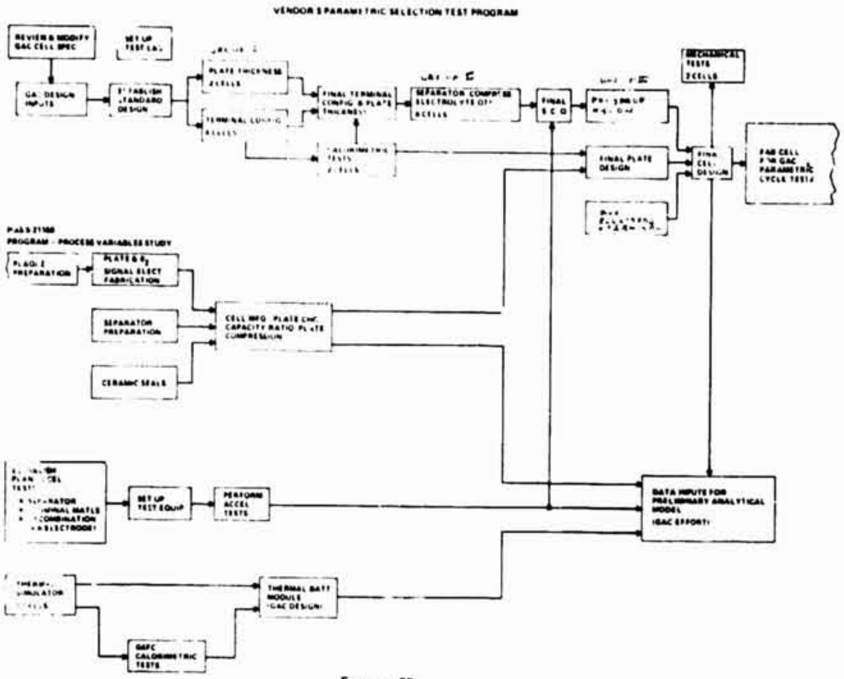


Figure 85

Figure 88

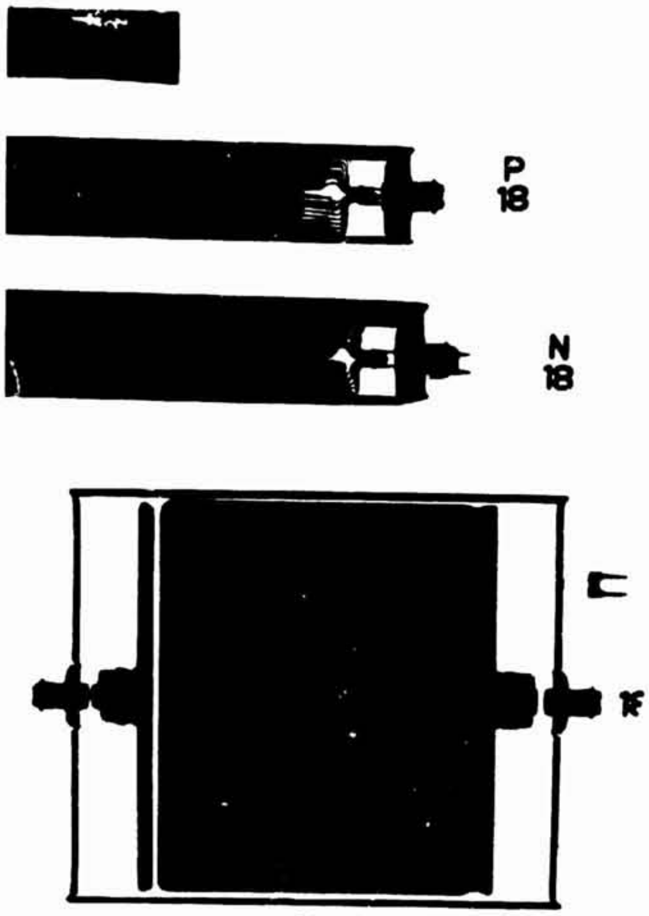
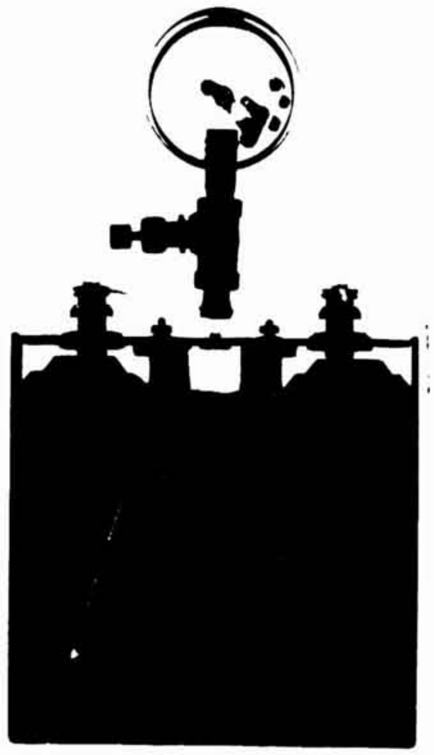


Figure 86


NICKEL CADMIUM CELL S_N 20
Figure 87

eb32

And we have used the process -- some of the inputs from the process variable studies to obtain a more uniform performance.

(Slide 89.)

I just happened to have this slide. It gives you an idea of what the thermal module looks like.

We have four cells which are put into this in an aluminum container. It was designed mainly for thermal reasons and our thermal engineer will be here tomorrow and if you have any questions you can go into that.

It will do the job on the design restrictions, the design conditions which we have. Essentially it's a box, it's an aluminum box which is anodized. Each cell is wrapped in teflon-- No, correction, in kapton, and then embedded in the container and a top restraining plate is put on top of that to act as a pressure vessel.

I want to point out one thing. We did discuss this morning and in the early afternoon on the amp hour terminal leak problem. We have not done extensive life cycle testing with this terminal, but these heater cells-- They have been constructed some of them as long as nine months ago, and we have not seen any leakage either from heater failing leak test or from the gauges. They all hold a high vacuum.

But at the same time we are investigating the possible terminal seal leak problem and we are dissecting some eb33 cells; not this. We want to hold this module. We need it for our charger checkout.

(Slide. 90.)

This is a plot of the capacity versus cycle number for the various cells which we've built, and I've combined group 1 and group 2 and I've averaged those numbers.

At the bottom you have a cycle number. Unfortunately I don't think it's too clear. The cycle number does not mean very much; it's just the way the cycles were conducted.

Below that we have a test condition and in the test condition we set up a parametric regime. All these were full cycles, full capacity cycles which we've conducted to variate these cells, and the regime essentially consisted of the-- The first group, the first nine cycles, were conducted 20 degrees C., which were the upper limits of our specification and the zero degrees C are the lower limits.

The first cycle consists of the conditioning which consisted of a 50 amp discharge, 10 amp charge, and then we had three capacity cycles which were conducted at 50 amp discharge, a 30 amp charge. Then we had a high rate discharge cycle which consisted of a 100 amp discharge and 30 amps charge, and then we had a high rate charge cycle which consisted of 50 amp discharge and the high rate charge consisted of a 30 amp charge to the voltage limit and -- No, correction, 60 amp

eb34

charge to the voltage limit and then a 30 amp charge against the voltage limit.

The next condition was a low rate discharge which-- No, low rate charge which consisted of a 50 amp charge and 15 amp charge. Subsequently, there was an overcharge test conducted where the cells were first charged to 30 amps to the voltage limits and then 10 amps for eight hours; then there was discharge at 50 amps.

Subsequently they received three orbital cycles which were conducted at the average depth of discharge of 30 percent. I should say under design conditions there is a minimal depth of discharge of 12 percent and maximum of 50 percent depth of discharge. And then afterwards there was discharge at 50 amps at one volt in each instance, and the same regime was repeated zero degrees C.

Now we had the following designs. We had two pre-contract cells which were actually thrown in because they were what I had available for comparison. The baseline design is more or less the standard design which consists of the 28 mill -- 29 mill electrodes. Then we have a thin plate design which consisted of about 22 mill electrodes. Because of the thin electrodes we could add two more plates to the cells.

Then we had the post terminal design which consisted of the baseline plates except the only change were the

eb35

terminals; of course also the higher cell case.

Then in addition we ran a baseline to cell in shims. We wanted to see the effect of the tightness of the pack. And before that we had a WX 1242 which is polypropylene material. The last two cells were polypropylene ST 2140 in combination with a woven polypropylene. Before that time this gives us the best stuff; the combination of the two would build up to the thickness of the nylon.

Now since we had slight variations in the active material I have normalized the data and put it on-- It can be seen on the next graph.

(Slide 91.)

I took the positive active material utilization in amp hours per gram times 10^{-3} -- This is a little nicer than percent, I thought -- versus the cycle number.

One can note-- Maybe I'll go to the next-- I averaged all these numbers. What is interesting here, with the polypropylene at the high discharge rate, we get a substantial dip.

If you look at the 20-degree data you will see in general a trend in the cell's -- in the active material utilization was about a 20 at zero; that is zero for all cells, but especially the polypropylene separater at the high discharge rate we got a substantial dip, a relatively poor performance.

eb36

However, I must add that the polyprophylene did not receive a heat treatment which they sometimes do for heat sterilization and which I've seen some information increases their capacity somewhat. That was not done on these two polypropylene designs.

92

To analyze the data a little bit further, --

(Slide 92.)

-- I have averaged for the 20-degree C. data and the zero-degree data the utilization for each cell design. It clearly shows that the thin plate design, which is this one and this one -- I don't know why it doesn't come out a little bit clearer. Well, this one is the thin plate design. The utilization was the best compared to all the others.

The pre-contract cell did pretty well at 20 degrees C.; it did not do so well at zero. The baseline design and the opposed terminals and the cells with the shims performed essentially the same at 20 degrees C.; at zero degrees C., the baseline design was somewhat superior to the opposite terminal and the ones with the shims.

The FT 2140 and the warm polypropylene did not perform too well at all.

(Slide 93.)

We conducted some ratio tests to get some idea what the positive-to-negative ratio is and what the pre-charge adjustment is. In all instances we would have liked to see

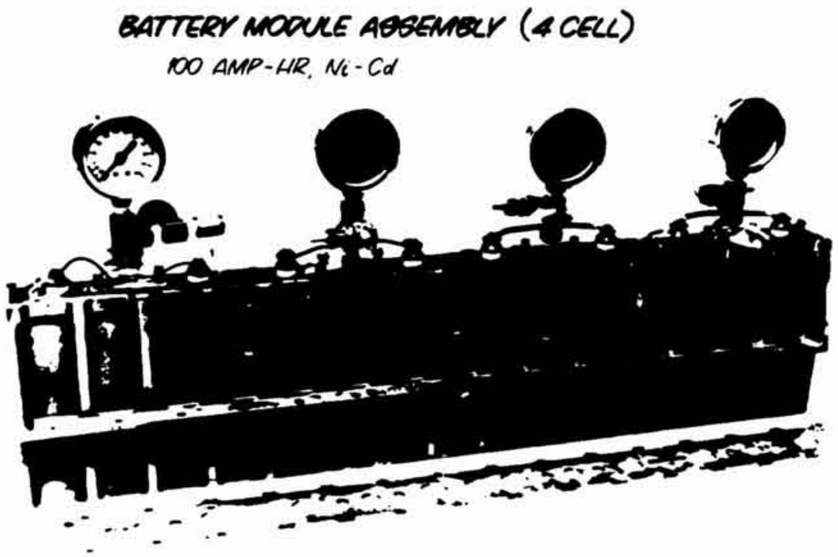


Figure 89

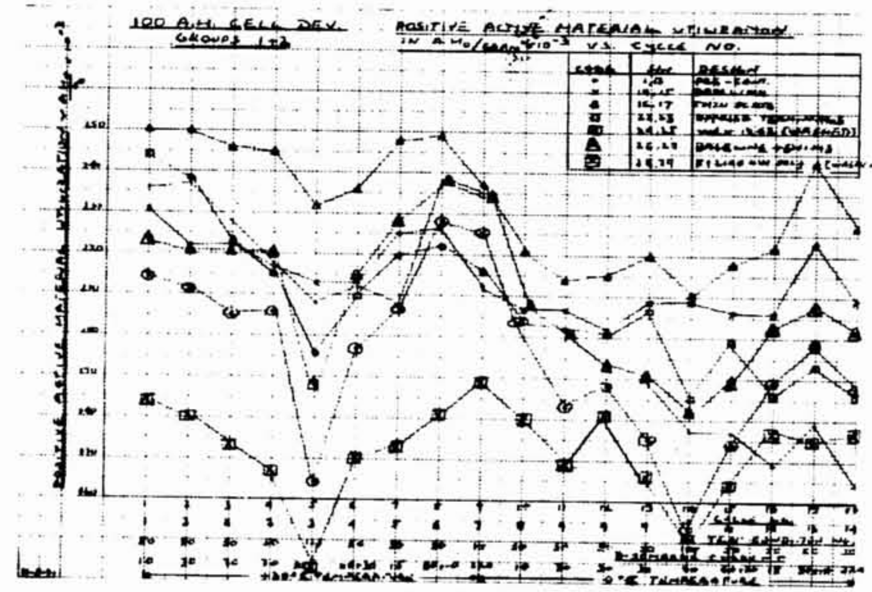


Figure 90

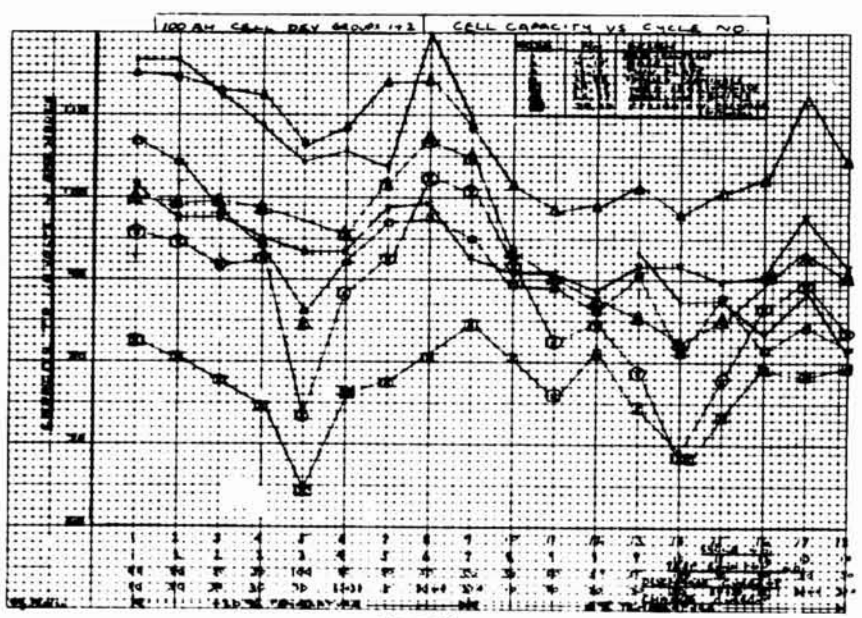


Figure 91

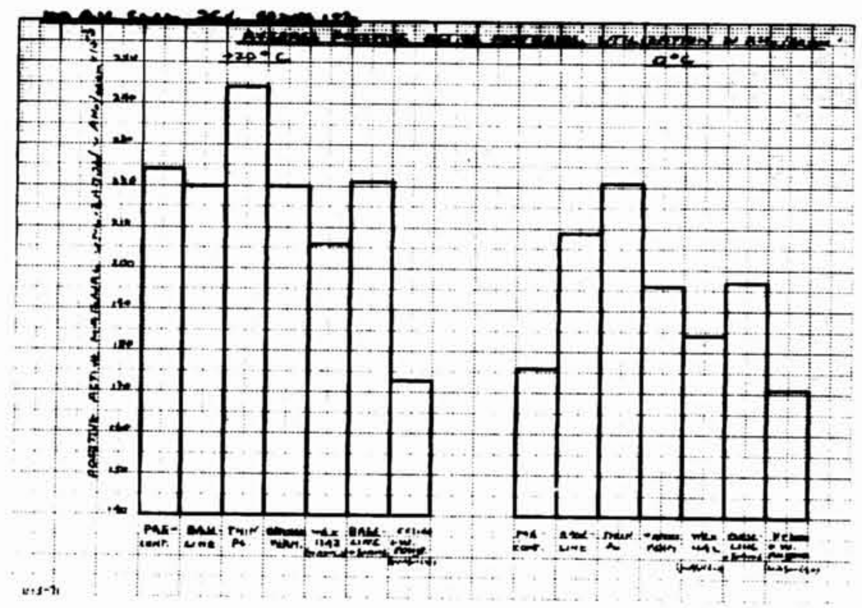


Figure 92

eb37

a ratio of 1.5 minimum. We have seen that. The pre-charge was somewhat high; some cells were even higher.

What we have done in cell 14 and 17, we gave the cell some overcharge and then put it in a centrifuge to reduce some of the electrolyte and the overcharge was conducted while the cell was open so therefore that precharge was changed so we cannot use that too much.

Even then the precharge was somewhat high. We'd like to shoot for a lower number in future cells.

(Slide 94.)

We did conduct some carbonate impurity analysis whereby we know what the analysis of the electrolyte is at filling and we analyze the electrolyte -- again what we took out by this centrifuge technique and we found a substantial pickup in carbonate from what we had initially.

We somehow feel that the carbonate must be contributed from the plates. Apparently it is introduced initially and it's something to be watched out for. Apparently plates during the duration of their affect must be washed thoroughly; maybe they have to be kept in an inert atmosphere during shipment or in sealed containers during shipment. It could contribute to a high carbonate content later on.

(Slide 95.)

This is the change in the terminal design which we'd like to see in the finalized cells to reduce the torque

eb38

stresses. Now when you connect your intercell connector you don't apply any torque stresses through the ceramic which is delicate.

(Slide 96.)

This one is a sketch of the finalized module with these terminals. You see head coming out here. We didn't show the intercell connectors but this is how the intercell connectors are being placed on.

I have many more results. I couldn't present them all because it's too lengthy. In cell group 3 we have used two additional polypropylene separators and one of them is the Hercules which we thought looks interesting, and the other one slips my mind right now.

What's the second separator which we use?

CARR: Earl Carr, Eagle Picher.

In the next group of cells which are being -- well, they're about to be closed right now, there are two cells with the Hercules separator as described by Tom Hennigan this morning, and two cells have the thickest version of the new Pellon domestic polypropylene.

GASTON: Thanks, Earl.

I just wanted to add, on the opposite terminals there were some good results achieved with this. Several years ago some large, signficant differences were found but we didn't find them this time and possibly it was the internal

Ratio Test Results from Dev. Groups 1 + 2 Sample Cells

Item No.	Cell S/N	Design Description	I_0TN1 (AH)	I_0TP3 (AH)	I_0TN3 (AH)	I_0TN2 = I_0[(TN3)-(TP3)-(TN1)] (AH)	Ratio = $\frac{TN3}{TP3}$	% Pre-Charge = $\frac{TN1}{TN3-TP3} \times 100$
1	14	Baseline	54.3*	118.5	182.5	9.7	1.54	84.8*
2	17	Thin Plate	22.5*	126.0	215.0	66.5	1.71	25.3*
3	26	Baseline + Shims	37.5	112.5	195.0	45.0	1.73	45.5
4	29	Baseline, except PT 2140 + woven polypropylene	37.5	112.5	176.0	26.0	1.56	59.0

Note: * Cells S/N 14 + 17 had received a number of overcharges during the electrolyte removal when cells were overcharged and gases escaped and subsequently placed in a centrifuge in order to lower the electrolyte quantity. This procedure has changed the original precharge settings on the negative electrodes.

Figure 93

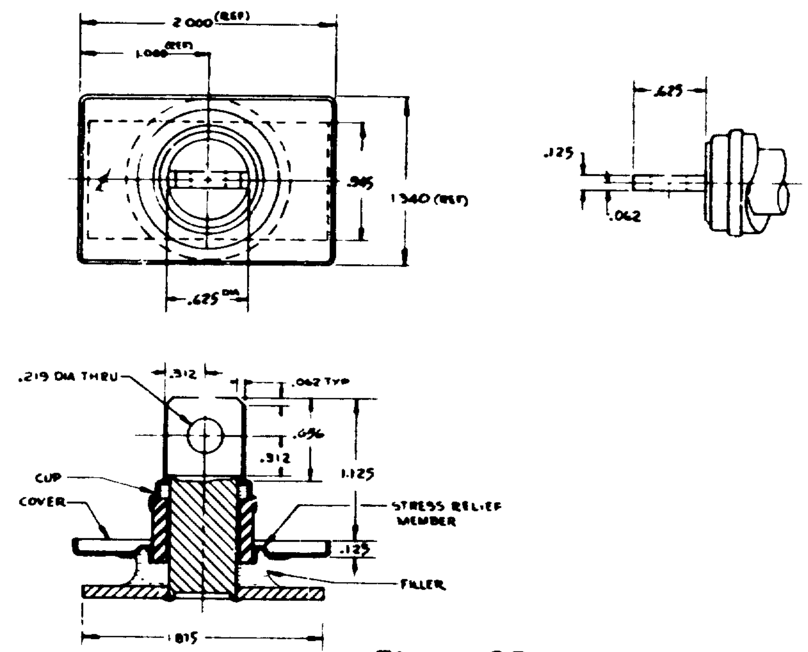


Figure 95

CARBONATE IMPURITIES ANALYSIS—ELECTROLYTE

106 AMP-HR CELL S/N 1

ANALYSIS CONDITION	% TOTAL ALKALINITY	% KOH	% K_2CO_3	K_2CO_3 (gm/liter)	K_2CO_3 (gm/cell)*
Electrolyte before filling	30.33	30.29	0.04	0.4	0.2
Electrolyte removed from cell	28.08	18.61	9.47	102.8	42.2
Change	-2.25	-11.68	+9.43	+102.4	+42.0

*Dissolved in Electrolyte Solution Only.

ANALYSIS BASED ON:

- Pre-Contract Cell, S/N 1
- Double End-Point Titration Method
- Electrolyte Removed After Other Testing

Figure 94

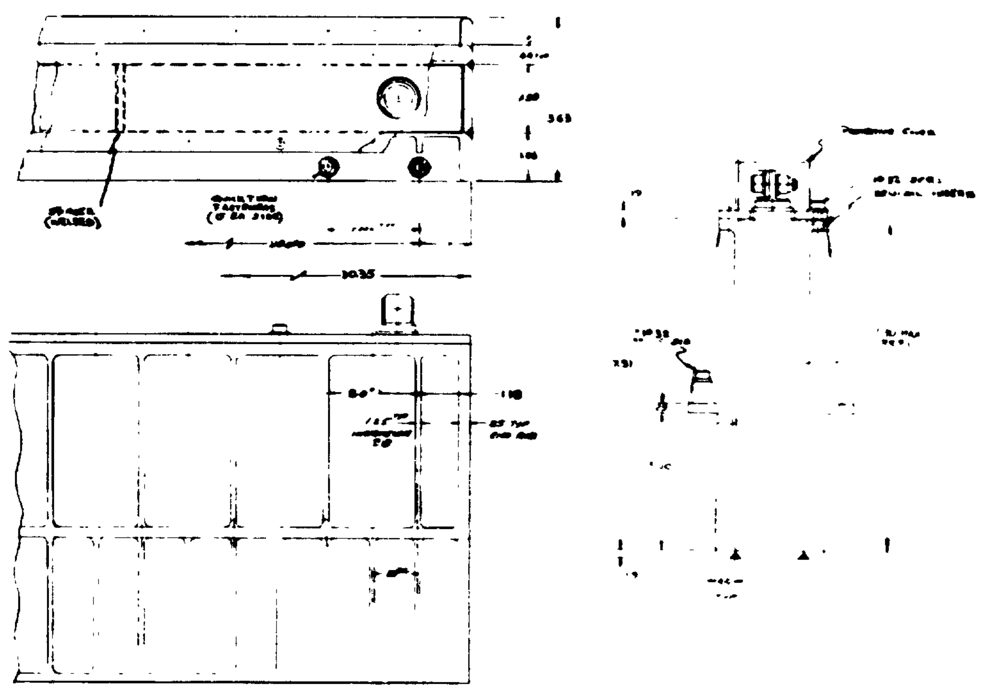


Figure 96

eb39

cell design where we feel a large weight penalty would be put on the cell and the module at the opposite terminals and we just didn't see an advantage.

So I can bring the module over here if somebody would like to look at the mockup.

WROTNOWSKY: A quick question?

GASTON: Yes?

WROTNOWSKI: Art Wrotnowsky, GAF.

Would you please discuss the potential range of the cell stack pressure expressed in psi that you have in mind for your design?

GASTON: The --

WROTNOWSKI: Stack pressure or compressional stress, the possible range that you might use?

GASTON: I don't have it with me right now. I would have to defer it to a later point.

WROTNOWSKI: Might you use heavy -- high pressure or must it be loose?

GASTON: We don't want too high a pressure. We've found where we added the shims at zero degrees C., we had a poor performance compared to baseline. Also, in addition, with a high pressure, the plates would like to bow.

If you have a high pressure in the cell-- By "pressure" I assume the packing effect -- then if the cell cannot -- if the plate cannot bow in one direction it will

eb40

bow up or down on the edges, and there is that danger.

Also, if we have it packed too tight, then the recombination is going to be affected. You're going to have poor recombination, so you have to try to compromise.

WEBSTER: Bill Webster, Goddard.

Steve, one question. Was your opposite terminal cell also an Eagle Picher cell?

GASTON: Yes. They were all built at the same time, the same type of plates, all Eagle Picher cells; right.

GROSS: Sid Gross, Boeing.

It wasn't possible to read all the detail on the slides you had, Steve, and I wonder if you-- The main conclusions that you came to on the configuration variables -- I didn't get all of them. For example, what did you conclude on electrode thickness? This was one of the variables.

GASTON: All right. An electrode thickness-- At the moment we favor the thin design, although --

GROSS: Did you get some data to prove that it's better?

GASTON: Yes. I didn't bring the voltage data but I have the voltage data and the utilization data. With the thin plate design, the utilization was considerably better with the thin plate design at both temperatures.

Also, I have the orbital information. We don't see any gain --

eb41

GROSS: They report plotting relative performance rom the left on the Y axis, --

GASTON: I wouldn't say --

GROSS: -- some relative term?

GASTON: I wouldn't say relative term. It's in amp hours per gram based on the positive active material and I assume all cells are positive limiting at charge and discharge and the ratio results show this.

So therefore, I normalized all the cells, based on the positive active material.

GROSS: Can you point then to the thick electrode and the thin electrode?

GASTON: Okay. The first column are the pre-contract cells which happen to have thick electrodes. Then the baseline cells are thick electrodes.

This one is a thin electrode. We have the opposite terminal. We chose at that time to use the baseline electrodes without the terminals; the same thing with the WX 1242. It was the baseline design with this polypropylene separator material. The baseline design with shims; it was the intent possibly to have a tighter pack, to add two more plates. However, with shims we found that the lower temperature performance was quite good and we are somewhat concerned about the bowing of the plates and having tight design might lead us to premature failure.

eb42

The FT 2140 also had baseline plate, polypropylene. Again pre-contract baseline thin plates, opposite terminals. WX 1242 baseline and shims, FT 2140.

GROSS: Okay. So the three -- the four -- If I look at that correctly, the four lowest performers were polypropylene separator -- is that right?

GASTON: These two types, yes. These two types, this, this. Of course it depends on what temperature you're talking about. The very lowest, the 20 degrees C., is the FT 2140 which also had a woven polypropylene.

The next lowest was WX 1242. Then for all the others it's an even toss; they performed identical.

Now at your low temperature-- The lowest was the FT 2140 with the woven polypropylene. The next lowest was the pre-contract cell.

Now the pre-contract cells had a little different design. They had a little more electrolyte. They had something like 23 percent based on the weight of electrolyte to the core weight ratio. So whether this was a contributing factor, I don't know. But at low temperature the pre-contract cell performed the next lowest, and then it's the polypropylene.

Now we chose-- In the group 3 cells we chose different polypropylenes and if necessary, we might want to give a heat treatment like is being done in heat sterilization.

eb43

I will look into it a little more closely if the performances are still poor.

GROSS: You said also that you investigated the effect of pack pressure. What conclusions did you come to there? That's the shims.

GASTON: That's the ones with shim.

GROSS: Okay. So you concluded that --

GASTON: Tighter packed at 20 degrees C., we get a pretty good performance. However at lower temperature, a low performance. In addition, I'm a little bit concerned on making the cell pack too tight.

So far what I concluded is that the thin plates are the best plates though we still keep standard plates as a control in the next group. We have to eliminate the opposite terminals and of course we have eliminated so far the 1242 and the FT 2140 polypropylenes. These two polypropylene materials we have eliminated.

GROSS: Okay. You have eliminated the opposite terminal design on the basis of weight or performance?

GASTON: We take a look at both. The performance at 20 degrees C. is pretty good; at low temperature it is not that good. But it's a large weight penalty you have to pay, from 8.8 to about 9.5 pounds. So unless you get a real superior advantage for the opposite terminal design I wouldn't want to go that way.

eb44

GROSS: Thank you.

FORD: Steve, I think you could clarify one point. On the Y axis you have ampere hours per gram. Is that cell weight or core weight or what grams is that?

GASTON: It's ampere hours per active positive material, active positive material.

DUNLOP: Jim Dunlop from Comsat.

That's my question, but I want to clear it up a little more.

The number is-- I still can't read it, so will you tell me what the ampere hours per gram are, what the number is up there?

GASTON: Okay. I apologize. I thought it would be a little bit clearer.

I put on the axis 10^{-3} so whatever the values are, it's 10^{-3} so that's 223 on the 23 degree C. data. For the pre-contract cells I have 223, or .233 if you take 10^{-3}. For the baseline we have 220; for the thin plate we have 244; for the opposite terminals we have 220; for the WX we have 206; for the baseline and shims we have 221; for the-- Did I skip one? No.

For the FT 2140 with the woven polypropylene we have 173.

Now these are the averages for two cells for all the conditions which I conducted tests for which I had pointed

eb45

out in previous slides.

Now for zero degrees C. for the pre-contract cells-

DUNLOP: That's enough. I think I can get it off now.

Let me ask another question now. To relate this, since I can't remember off-hand the conversion, if you assume that your nickel is going from the three-valen state to the two-valen state or something like this,--

GASTON: Yes?

DUNLOP: -- how much does this represent in terms of percentage --

GASTON: Percent.

DUNLOP: -- of the theoretical?

GASTON: I don't recall the number off-hand. I think somehow that 260 is the theory. I wouldn't want to make that statement. I didn't bring that number along.

DUNLOP: Okay.

GASTON: Is there anybody who can help us out in that respect?

GINER: 289.

FONT: 286.

GASTON: 286.

DUNLOP: So you're really saying up there that 240 represents about an 85, 90 percent utilization, --

GASTON: Yes.

eb46

DUNLOP: -- something like that?

GASTON: Yes, I think that's pretty good. I don't know whether we can do a lot better.

CARR: Earl Carr, Eagle Picher.

Just one other thing I'd like to point out and that's in the charge regime, we charged at a constant current to a voltage cutoff. This is the way all the cells were charged. They were charged to 1.51 volts at 20 degrees C. and they were charged to 1.58 or 1.57--

Do you remember the numbers, Steve?

-- at zero degrees, something higher than --

GASTON: It's 1.57.

CARR: And then the other thing is that the reason for the lower utilization at zero degrees C. is because the cells such as the pre-contract cells which were just shown reached their voltage cutoff quicker and in that case they were wetter cells which is what you would expect.

VOICE: What was the cutoff voltage?

CARR: 1.57 at zero.

VOICE: What about discharge?

CARR: Oh, on discharge one volt.

GASTON: One volt. All the capacity was measured to one volt.

STEINHAUER: Steinhauer, Hughes.

You have an interesting packaging design. I was

eb47

wondering if you could tell us approximately what percentage of weight is contributed to the packaging and to the cell?

GASTON: I think we have the ratio 1.4 to 1. You've got to realize in this design, safety is the first consideration because it's a manned crew. Also, thermal control is a consideration, so I think we can get a more optimum design at a later point.

And one of the reasons is right now we have-- The cell cases are still hand-made. We have tolerances-- I shouldn't say "hand-made." They're not drawn containers; they're welded containers. You have tolerances on that and when we make the battery container we'll have to design for the thickest or for the largest tolerance.

Subsequently, if we can go to -- If drawn containers becomes a flight program, then we can make the module smaller and get a more beneficial weight ratio.Right now this gap is f.lled up with putty, thermally conductive putty.

STEINHAUER: And then specifically you have this aluminum on the outside.

GASTON: Yes.

STEINHAUER: Is that the 1 - 4 --

GASTON: Right.

STEINHAUER: -- factor that you're talking about?

GASTON: Right.

Now this top is a dust cover which could be changed

eb48

to a hermetically sealed container if that becomes necessary. That decision has not been made at this time.

Also, they chose the O-terminal configuration. It has a quick connect-disconnect mechanism. The surface has to be flat. Of course that is going to be facing the cold well, the cooling well in the space station. So that there are a whole number of considerations because this is a specialty package for a manned application.

WROTNOWSKY: Wrotnowsky again, GAF.

On the WEX 1242, I believe that Eagle Picher leached the --

GASTON: Yes. I should have added all these polypropylene separating materials have been washed, I think three times, in --

WROTNOWSKY: You know the Canadians have a similar material in flight still operating after seven years. This was not leached. We don't suggest that you leach it. You're going to develop non-wettability and resistance.

GASTON: Well, we had-- Several years ago we had a problem on the nylon with the addition of wetting agents which apparently showed up after a considerable number of cycles. I am somewhat concerned about the addition of wetting agents and I prefer not to use any.

FORD: Okay, we have to stop for a moment in order for the recorder to change his tape.

#5

In addition, I would like to make a comment I made earlier before the meeting got started.

On the table to my left, and to your right, are two black notebooks labeled "Photographs of failure analysis of nickel-cadmium cells, Vol.I, Vol.II." This is a group of photographs we have accumulated mainly from the Crane test program over a period of several years, some from the Goddard test. There are some very interesting results that you can find from looking at these photographs. It covers all manufacturers. There are all types of failure illustrated. Please, at your leisure, this afternoon or tomorrow, feel free to leaf through them.

If there is time tomorrow in the discussion, there are some specific photographs I hope to be able to put up on the board for further discussion. Because it is my opinion that we have identified a further limitation on the nickel-cadmium cells, once we saw separator problems, seal problems. We're getting down now to the basic plate construction and how it's deteriorating with life. And, believe me, I don't think you can get any more basic than that.

VOICE: What does the schedule look like for tomorrow?

FORD: The question is, What does the schedule look like for tomorrow? If you will bear, and indulge with

wb2

us, we have two more presentations for this afternoon, which will finishup this particular aspect. In the morning, I believe it's on materials. And also we cover thermal.

Our plan at this point is to get through as early as possible, such that we can let people leave that have to meet schedules. And those that would like to stay around for further discussion and rehash some of the things that we've gone into, we will do that also.

So the idea is to finish as much of the formal presentation as possible, perhaps by noon tomorrow.

Okay, if we could get back to the presentation.

As I mentioned earlier, we have some questions regarding.... As you all know, we have been taking quite a bit of data, quality assurance data, test data, during the process of the OAO program in manufacturing flight batteries. This started early in 1968, when we started on the earliest flight batteries for the A-2.

We have a gentleman here from Grumman Aerospace who will present some performance data on the A-2 flight. I will complement that after he is finished with his presentation.

What does all this data mean to us? How can we use it? Why are we taking it?

It's time we took a look at that.

Right now I would like to introduce Joe O'Rourke from Grumman Aerospace Corporation, who would like to address you on several topics. One is on A-2 flight data performance, capacity, and flight weight screening, and the relationship between the electrode capacity ratio test that is required in the specifications related to manufacturers' data. And then all this is related to a contract that Grumman has in regard to the OAO program, which is a data analysis program to go through an analysis, to regression, and make some predictions and see just what all this data is meaning to us today.

At this time I would like to introduce Joe O'Rourke.

xzyz

O'ROURKE: As Floyd mentioned, there has been quite a bit of data generated along the 20-ampere-hour nickel-cadmium cell line as a result of the OAO satellite program. Unfortunately, the OAO program is starting to phase down now. So we all thought maybe it would be a wise thing to get hold of all of this data and put it in some handbook fashion so that it would be of benefit to anyone interested in ni-cad batteries at a later date.

(Slide 97.)

This is essentially an outline of the areas that I'll be looking into on the data analysis program.

Under process controls, one thing I will be looking at is documenting the chronology of the OAO cell spec development.

wb4

Essentially this contract starts with a battery that was built in the summer of 1968, and that is the battery that is up in the A-2 satellite right now. And, as I will show you later, it's performing well beyond our expectations.

The chronology of the cell specification will begin, the development of that will begin right there. Essentially that particular specification for that battery was an outgrowth of the NASA Goddard interim spec which was developed. And before that time there weren't many tight controls on building the cells that are presently in there. So I will be documenting that.

Under cell component analysis I will be looking at such things as the plate data from SAFT. I have another vu-graph right here.

(Slide 98.)

Essentially what this is is -- you see up at the top the serial number 25A and 26A. That's the two batteries that are in the space vehicle right now. 32,33 were two batteries after that. 34 and 35 was built last summer. And for reference I have plates, data on plates from the ATS program.

Essentially what I was was, I took the initial SAFT capacity, and that is made on a 1 decameter squared sample of plate, I believe, a 1 decameter squared piece of plate, I believe. It's tested for capacity purposes. What vb5

I did was, I took the data, ampere meters per decameter squared, multiplied it by the area of the plate. And we used nine positive plates in the cell. And I multiplied that out to come up with an equivalent of 20-ampere-hour cell capacity.

The figures given are the ampere hours, negative plate ampere hours for the SAFT capacity.

Then we do a formation discharge during the processing, and we see that the negative plate capacity there is around 97 or 98 percent of what it is calculated to be from the initial SAFT sample.

Then for the OAO we take three ratio samples. One right after formation, one after the plates are rinsed, washed and dried, and then we do a final post-production cell ratio.

I guess the interesting thing here is to see that the ratio -- that the capacity has increased. Post-formation it's somewhere around 112 to 114 percent of what it was from the SAFT sample. The post-rinse, somewhere around 112 to 117. And the final cell, we're seeing somewhere around 106.

So we're seeing a net increase in negative plate capacity.

(Slide 99.)

Okay. This is the same thing with the positive

wb6

plate, starting out again with the initial positive plate capacities.

Notice from the SAFT data they are very close to what the negative plate capacities were.

During formation it drops considerably. And when I say "drop," we may not really be seeing a loss in capacity. The SAFT cycling technique is different, they are using different charge and discharge rates. And that may account for some of this.

But from formation down to ratio we're essentially using the same type of charge-discharge regime. And we're seeing final ratio positive capacity around 83, 85 percent of what it was calculated from the initial SAFT capacity.

So the initial ratio that SAFT may show may be very low, but when we do measure our final ratio in the cell we can be up -- if we start with something around a ratio of 1 we could end up anywhere between 1.3 and 1.4, something like this.

Okay. Well that was one thing that I looked at in the cell component analysis.

Also included in here will be documentation of any separator tests and KOH analyses which we made also.

Another thing included in here with the last battery build, the one built last summer, we started screening the

wb7

plates as they came in on the basis of weight. Gerry Halpert did a study showing that if we screened the plates initially we would be getting tighter capacity groupings.

(Slide 100.)

And that is essentially verified here.

The three batteries prior to the one built last summer, the capacities are essentially very close to being normally distributed about a mean. The 25A, 26A mean cell capacity was 25.46, and one standard deviation was .62 ampere hours, and a total range of 2.83.

The next one, cell No. 30,31, had a mean of essentially the same, 25.63 ampere hours. By the way, these two battery builds used the same SAFT plate lot, so you would expect to have about the same average capacity and same standard deviation; which they do.

Each battery assembly, which this represents, -- although there are sixty-six cells in a battery, when the vendor makes the battery they make around 150 cells; and that's what these distributions reflect, the total of all the plates for 150 cells.

Turning to 32, 33, it had a mean of 26.22 ampere hours, and a standard deviation of .51. Range, about the same, 3.68, as 30,31.

Now 34,35, which was built last summer, we screened the plates as they came in. And although the capacity, the

OAO DATA ANALYSIS PROGRAM

I. PROCESS CONTROLS
- o CHRONOLOGY OF CELL SPECIFICATION DEVELOPMENT
- o CELL COMPONENT ANALYSIS
- o FABRICATION DATA

II. CELL PERFORMANCE
- o ELECTRICAL TESTING
- o MULTIPLE REGRESSION ANALYSIS

III. BATTERY PERFORMANCE
- o ACCEPTANCE TESTS AT GRUMMAN AND GSFC
- o COMPARISON WITH COMPUTER MODEL

IV. LIFE AND SPECIAL TESTS
- o CRANE
- o GSFC
- o FAILURE ANALYSES

V. A-2 FLIGHT BATTERY EVALUATION
- o 30 DAY SUMMARY
- o COMPARISON WITH ACCEPTANCE TESTS
- o INITIAL VS. RECENT PERFORMANCE

VI. CONCLUSIONS AND RECOMMENDATIONS
- o CHARACTERIZE 20 AMPERE HOUR NI-CD CELL
- o CELL SPECIFICATION MODIFICATIONS
- o IDENTIFY KEY PARAMETERS
- o SPACECRAFT CONTROL METHODS

Figure 97

CAPACITY DATA - NEGATIVE PLATE

	S/N 25A, 26A	32,33	34,35	A.T.S.
I. SAFT CAPACITY (Ah/dm^2 × .91 ∂m^2/plate) x10 plates/cell	(100%) 37.95 AH	(100%) 37.95 AH	(100%) 37.31 AH	(100%) 41.95 AH
II. FORMATION (Final discharge capacity)	–	(97.25%) 36.91 AH	(97.07%) 36.22 AH	(98.18%) 41.19 AH
III. RATIO	(114.00%)	(111.98%)	(114.44%)	
A. Post Formation	43.20 AH	42.50 AH	42.70 AH	–
B. Post Rinse	–	(112.25%) 42.60 AH	(117.39%) 43.80 AH	
C. Final Cell	–	(106.06%) 40.25 AH	(107.96%) 40.28 AH	(105.00%) 44.05 AH

Figure 98

CAPACITY DATA - POSITIVE PLATE

	S/N 25A, 26A	32,33	34,35	A.T.S.
I. SAFT CAPACITY (Ah/dm^2 .91 m^2/plate) x9 plates/cell	(100%) 34.40 AH	(100%) 35.25 AH	(100%) 31.94 AH	(100%) 35.00 AH
II. FORMATION (Final Discharge Capacity)	(82.99%) 28.55 AH	(82.52%) 29.09 AH	(81.74%) 26.11 AH	(80.71%) 28.25 AH
III. RATIO				
A. Post Formation	(90.20%) 31.00 AH	(91.63%) 32.30 AH	(92.04%) 29.40 AH	–
B. Post Rinse	–	(88.51%) 31.20 AH	(87.66%) 28.00 AH	–
C Final Cell	–	(82.78%) 29.18 AH	(83.90%) 26.80 AH	(88.00%) 30.82 AH

Figure 99

EFFECT OF PLATE SCREENING ON CELL CAPACITY

PLATE AVG. WT. ±3.5%

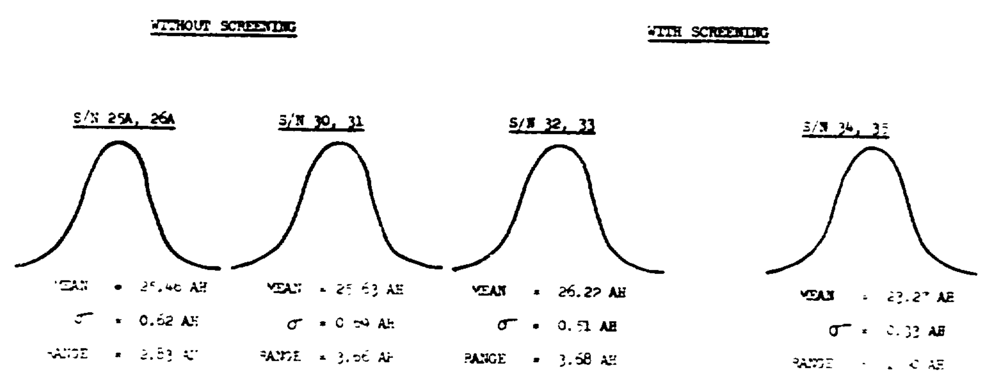


Figure 100

wb8

positive plate capacity was -- which we expected -- the total range and the standard deviation about the mean was significantly decreased. The standard deviation here was .33, which was almost half of what it was in some of the earlier builds. And the total range is about half what we saw before, also.

(Slide 101.)

Okay. During the formation cycle -- what I presented just before was during a final discharge capacity cycle. This here is during formation when they measure the positive plate capacities. And we see the same decrease in spread of capacity here.

For 34,35, which is with the plate screening, the one standard deviation is .335 ampere hours. And for 32 and 33, without plate screening, it was about double that, about .6 ampere hours.

(Slide 102.)

This I thought was interesting. This is the negative plates during formation. And what I see here is, we don't have the decrease in capacity spread like we did on the positive plates. I don't know whether Gerry Halpert found this to be true on his negatives or not. But this is, again, for each serial numbered battery there, and each distribution reflects a sample of probably well over 200 formation packs.

So the sample size is significant enough to call it b9

significant.

The spread here, the standard deviation for the one with plate screening, is actually slightly higher ampere hour capacity, almost enough to say they're the same, actually. But we're not seeing the range being decreased like we did with the positive.

(Slide 97.)

Okay. Continuing along with the data anlysis program:

Under cell performance we have a lot of data generated during electrical testing now. What I'm looking at on the electrical testing is such things as the formation, the ratio tests, the capacity cycles, the overcharge data that we run during the vendor testing, and pre-charge.

I did find something out to do with pre-charge, but I guess I'll save that for tomorrow when we're going to have a session on pre-charge.

This thing I found on pre-charge was the result of -- I'm also using a multiple regression technique, which is similar to the one being used by Eagle Picher in their process variable study. Essentially I'm taking the data -- the variables, the data that we took on cell variables, and I'm regressing them again to dependent variables. In this case, the one I did was, I was regressing the intrinsic cell variables against the amount of oxygen generated during

wb10

pre-charge which we measured on the last build.

Under battery performance, we always, of course, run acceptance tests at Grumman, and Goddard runs another one on the vehicle prior to launch. And we have a lot of data there. And that's valuable in comparing it with subsequent flight data.

We have a computer model of the battery. And this isn't a simple mathematical equation with, you know, so many variables, you plug them in and you get a response. It's a dynamic computer model where you input into the model various conditions like the voltage you're going to charge to, the battery temperature, your charge and discharge rates, things like this. And by extrapolating between parametric curves, charge-discharge curves which are inside the computer program, it predicts, based on temperature and state of charge, and things like this, what your voltage and discharge profile will look like at any point in time in orbit.

I have with me a vu-graph which I'll show in a moment which compares the actual flight data and acceptance test data with the predictions by the computer model.

Under life and special tests, on the OAO there were quite a few OAO cells out at Crane which are going through a variety of regimes.

One thing we were looking at yesterday was, we have three packs of five cells each at Crane, where we are trying to evaluate what happens to a cell, or a battery under various storage configurations. Of course this is a very important item in the sense that once a battery seller delivers a battery, then the problem is if it's stored improperly and then doesn't perform up to what it was supposed to, that can raise all kinds of problems.

Essentially what you want to do is, if the battery performs well, or satisfactorily, upon delivery, you'd like to keep it that way until the flight, and hopefully have it perform that way throughout the flight.

We essentially have three packs out there, one which we stored shorted for six months. And I guess, Floyd you'll be presenting some of this data right after.

One pack we stored shorted for six months. Another pack we put on a trickle charge, a very low charge, a half amp, for six months. And the third pack we put through a series of charge cycles, discharge cycles, open circuit stands, to simulate what the battery would see during the vehicle integration and checkout; more or less a random electrical type regime.

We also have cells out there which we have had special pre-charges done, or modified pre-charges to. And we're evaluating the performance of those. And, of course, we also have cells which are undergoing life cycling tests, and we have some up to 19,000 cycles.

wb12

There are also packs undergoing special tests at Goddard.

I will also be including in this thing any failures, typical failure regimes that occur on nickel-cadmium cells that have occurred on the OAO cells.

I will be looking at the A-2, an evaluation of the A-2 flight. There was a 30-day summary of how well the batteries performed which I will be including in there.

And I will show you now a comparison between an actual flight cycle and how the battery compared during the initial acceptance test with the same type of electrical cycling and a comparison with the computer model also.

(Slide 103.)

Okay. The continuous line, the one with the circles and the dots in the middle, is actual A-2 flight data which was dumped at Rosman last Monday, Orbit 15,331. That is the profile. The battery temperature was 52° here, BVLS-4, which is voltage cut-off around 35 volts at 52°.

The x's represent the battery model prediction of how the cycle would be. And, as you can see, it compares quite favorably.

The triangles there are the data from the initial acceptance tests on the battery done at Grumman, with the same BVLS, the same temperature.

The only apparent difference that I see here is--

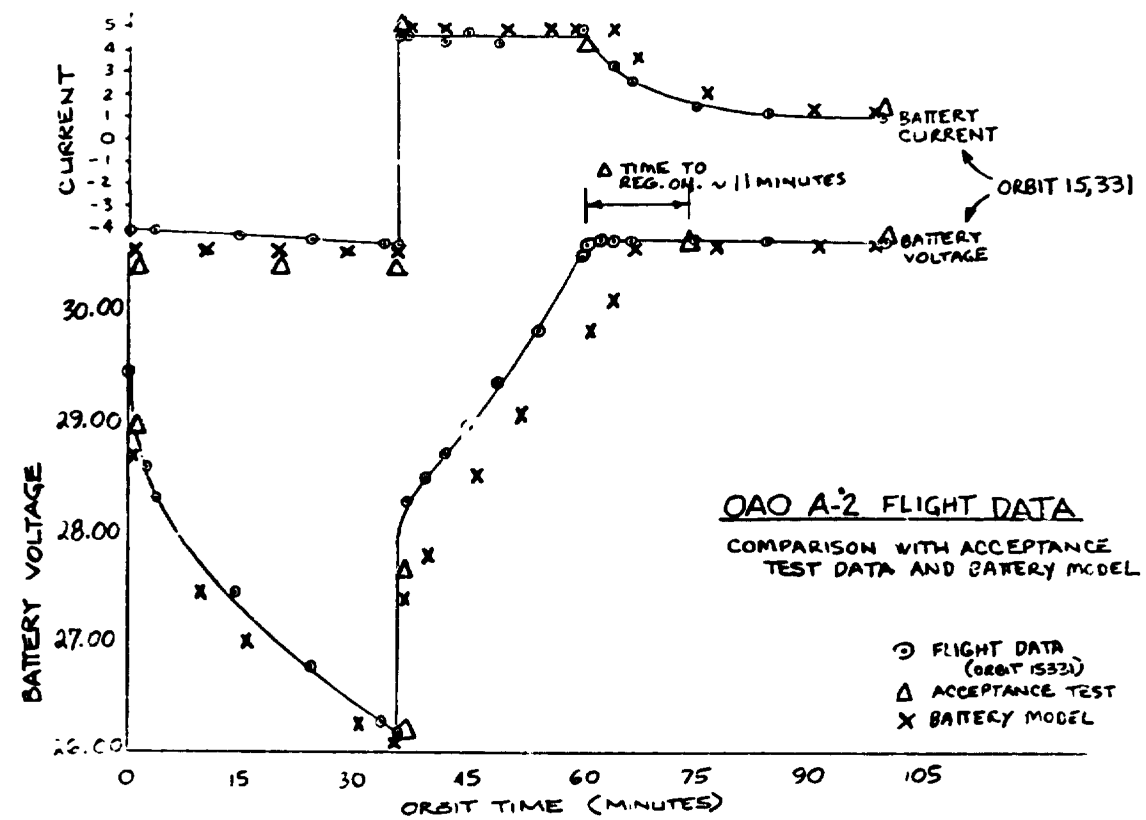


Figure 103

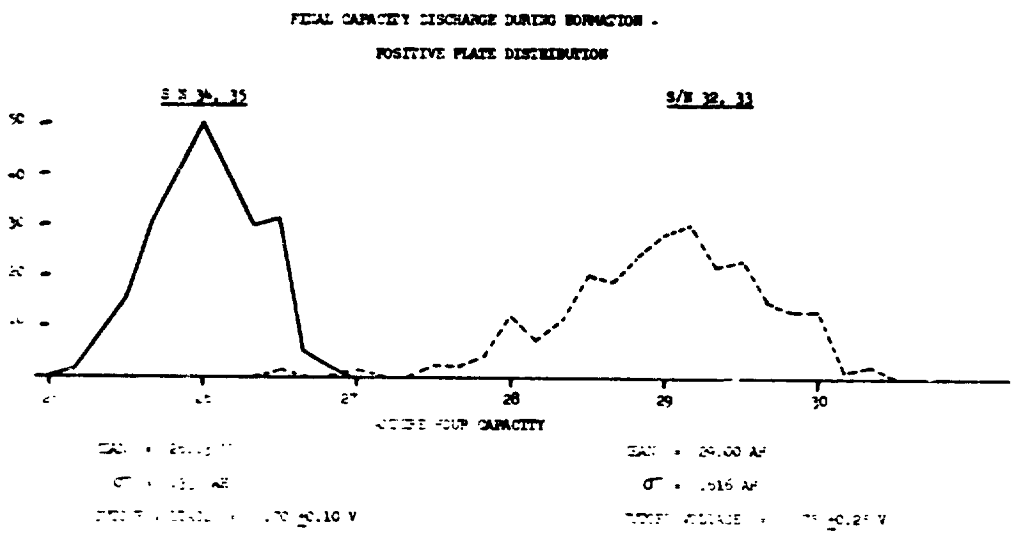


Figure 101

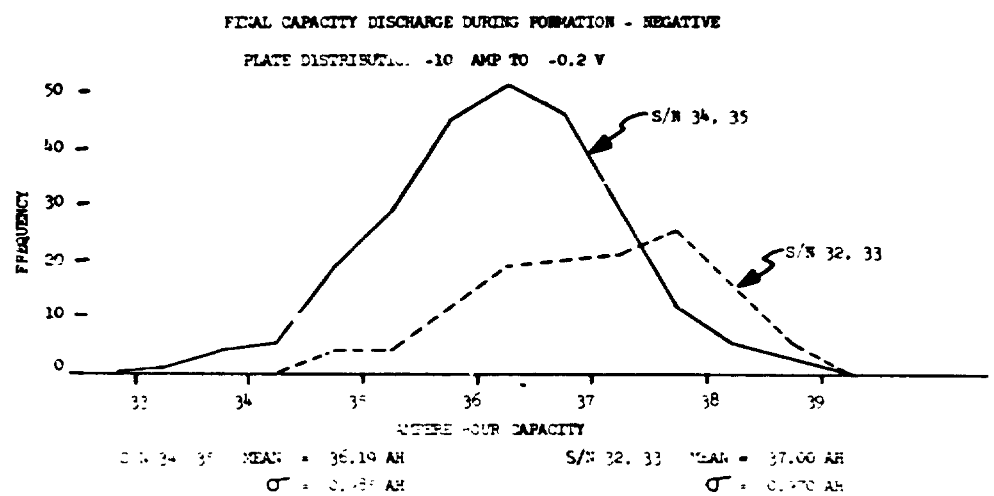


Figure 102

wb13

I want to explain that this portion in here, after the discharge, the battery voltage will increase until, depending upon the temperature, it hits a specified voltage limit. And when that happens the regulator comes on and keeps the battery at a constant potential.

Now what we're seeing here is, during the acceptance test, which is the triangle here, this is the point that the regulator came on during the acceptance test. In flight now we're seeing the regulator coming on approximately eleven minutes sooner. So the battery is charging with a higher voltage.

Essentially the battery model reflects this slightly. And it follows the current and discharge voltage profile rather well.

Okay. Then when this contract is completed certain conclusions and recommendations will be able to be made based on, hopefully, what we find out by tying all of this data together.

One thing will be to characterize a typical 20-ampere-hour nickel-cadmium cell. It possibly may reveal new features which we may want to incorporate in a ni-cad cell specification.

I might point out that one thing that I found on the pre-charge was already employed in the cell spec for the next battery build.

wb14

I hope to identify those key parameters which influence a cell's behavior. Possibly, hopefully -- as Floyd mentioned before -- be able to predict, based on the manufacturer's data, at that time anything that could cause a cell to fail earlier or have some adverse performance.

And, of course, of immediate concern is, if we do discover a problem, how could we -- what type of control could we employ on a spacecraft to bring that problem back into limits that we would desire.

Okay. Thank you.

FORD: Okay, Joe. Thank you.

We'll open the floor for questions at this time.

PASCHAL: Paschal, Marshall Space Flight Center.

In respect to your various storage modes, shorted out, cycled, and open circuit condition. What were your conclusions from this study?

O'ROURKE: Well, we just began looking at the data yesterday. It's really premature to make any definite conclusions.

We did see that on the cells that were on trickle charge for six months, they had higher capacities than they did at the vendor's testing. The cells that were shorted out had slightly lower, maybe an ampere hour capacity, than they did initially. And the cells that were on random type manipulation had capacities somewhere just a little bit higher than they were initially, but not quite as high as the ones that were on trickle charge.

So with trickle charge we did see a slight growth of capacity.

FORD: One additional observation was that the cell that had been on trickle charge did not show any increase in the overcharge voltage at 0°C., where as the other two packs, one being on storage and the other in spacecraft simulation test, both of those had to be terminated on overcharge because of hitting an upper limit of one-five-five, so they did not complete the 5-hour C/20 overcharge test.

All three packs went through this test initially.

So it is fairly early, it's only six months at this point. The program consists essentially of a six-month period with a re-running of a number of tests every six months. We're only at Step 1. We have at least a two-year goal on this program.

The information is available directly from Crane. For those of you who are interested, I can give you the pack numbers for identification, and it can be obtained from them directly.

DUNLOP: This is Jim Dunlop from Comsat

I have a comment and a question, and I'll give you my comment first.

I'm going to pre-empt myself here because tomorrow

wb16

in our pre-charge study, or presentation, we're going to present some data on cells that we've been running since 1969 in three different storage modes.

All we've been doing in that test is pulling out a cell every six months from every storage mode and running it through a complete chemical and electrochemical analysis.

There are three storage modes. One storage mode is trickle charge, and those cells are into their -- I think it's their six eclipse season, starting in about a week. And they're behaving rather well, frankly.

The cells that were stored completely passive with nothing going on during the storage mode, all developed high voltage characteristics during the last eclipse season. We have terminated that test because the utilization of the cadmium electrode apparently is not adding, itappears, any overcharge protection any longer.

The cells that are cycled every thirty days during the eclipse period and stored passive the remaining time are still behaving quite well; very similar to the cells that are on trickle charge.

That's the comment.

Passive is not with a short. Because we're really trying to run this test just like we run a-- It's just like Intelsat-4 is supposed to operate.

So what we do is, on the two passive modes, one is

wb17

charged, open circuit, and recharged every thirty days. That's very similar to the ATS F&G, I guess.

That mode is still working fine, by the way.

The other mode is the one where we discharge it down. It's then actually left open circuit, but to simulate the satellite -- the way the satellite is designed; it's pretty similar to most satellites; you've got the battery and solar array parallel to the telemetry load, so that you're always able to command the satellite. And that's a 12-1/2 milliamp load. So any time the battery would tend to try to operate above the solar array it would deliver this 12-1/2 milliamps.

So what it does, it pulls the battery down to the solar array voltage, which is about something like 1 to 1.1 volt per cell, and clamps it there. If it tries to go higher, it draws current; if it goes lower, it goes off. It just clamps it there.

It clamps it there in an almost completely discharged mode, in essence. But not with a short.

O'ROURKE: And did you have a question?

DUNLOP: The question is: I'm sure you must have been leading up to something when you said you had, in your pre-charge test you had uncovered something that you included in your spec. Now you're probably not willing--

O'ROURKE: I can't reveal it. Sleep on it.

(Laughter)

FORD: Jim, that's proprietary information you're asking for.

DUNLOP: How come it's proprietary?

FORD: Because we're it at Goddard. Joke.

(Laughter)

Are there other questions?

(No response)

Okay. Thank you, Joe.

Since I have designated myself to be last, I would offer you the chance to go home and not hear me, but you might take it. So I'm going to take about twenty minutes of your time. And I hope this will conclude those people who had asked to present something; with the exception of one person who said they would like to come back in the morning, since they're not totally prepared for it tonight.

As you know, in the last couple of workshop sessions, we have been talking about double plateaus, loss of discharge voltage with cycling, loss of capacity, and- - I'm going to use the word once and not use it any more today. --memory effect.

I would like to present some data today that we have accumulated through the OAO cell test program, which, as Joe has indicated earlier, has been quite extensive. But, quite frankly, I think we're a lot smarter today in

wb19

two areas: one, how to build a better mousetrap....or how to build a better battery, and, two, how to better utilize that battery once we've got it in space.

So without further to do I'm going to put the first slide up. It's very involved, so bear with me. And I would like to go through this slide step-by-step.

(Slide 104.)

When the OAO A-2 battery was built, serial numbers 25A and 26A, which is currently in the A-2 spacecraft, and which on December 7th will have completed three years in orbit, we iniated cell tests at Goddard on the flight cells to try to determine if those cells would meet our mission requirements.

In doing so, we initiated a cycle test on a 90-minute orbit, running at 15 percent depth of discharge and at 15°C. temperature.

The OAO spacecraft battery throughout 98 percent of its life has operated from the temperature range, in F., of 45 to 55°F.

I would like to call your attention to the first curve I have labeled '1.'

In the top is the first curve. And I will address each curve in the sequence of the numbers at the top of each label. In the bottom parentheses is the total number of accumulative cycles we placed on those cells in this cycle regime.

This cycle regime uses a voltage control, as implied earlier by Joe O'Rourke in his presentation. It uses essentially a current limit in the test, which is essentially a solar array limit in the spacecraft, until you reach a pre-set voltage limit. Then you go into a conventional taper and sit there and perhaps go into overcharge for the remainder of the orbit.

After 1636 continuous cycles we ran a capacity check, and this was conducted at a 6-amp rate. And, as you see, we have observed a fairly low discharge voltage. And what I have indicated here is a group of five cells. We have two test cells showing the spread across five cells. And it's interesting to note that this is approximately 24 ampere hours. This is a time scale; but if you divide the time scale by 10 you actually read ampere hours as well as minutes.

We subsequently recharged the cells by allowing them to cycle back up, again addressing ourselves as close as possible to the situation that the spacecraft would be in.

After recycling, under the same set of conditions, 28 cycles since the discharge of 1, we ran the battery back down, which is indicated by the dots, to assess the effect on the discharge voltage of that complete discharge of those cells. As was reported in previous literature, and as is obvious here, there was a significant improvement in the discharge voltage.

wb21

However, if you start looking at what's happening in the lower voltage range of cells, you see you paid a slight sacrifice in ampere hour capacity.

Now I point this out because that's what I'm going to conclude my presentation on. Because really what you see here is a difference in ampere hour capacity. But do you see a difference in the watt hour capacity?

After running it down the first time, 28 cycles, we went 110 continuous cycles. And then we ran another discharge to assess the effect of the additional 110 cycles; which, by this time, we were up to 3211 cycles total.

As you see, the discharge profile has begun to drop down slightly, and a slight decrease in capacity; but within the accuracy of determining capacity on cells and packs from cycle to cycle, it's approximately the same.

We allowed the cells to continue on cycling. And then we said, "Well that's what happens when you run a constant current discharge. But that's not what we can do in a spacecraft.

"What happens when you get into what they call a negative energy balance on the spacecraft? You cannot recharge the battery after each orbit, and on a period of several orbits you will run down in battery capacity to some low state of charge.

"Does this in fact enhance the subsequent discharge

wb22

voltage?"

So we set up the test where we plotted this in time, or really in ampere hours. We allowed the battery to discharge by just reducing the available charge current, similar to what would happen in a spacecraft when they got into unfavorable angles on the array.

And, as you see, on a cycle-by-cycle basis we began to run down. I point out that we accumulated approximately 1000 cycles before we made this run-down. This was 1000 cycles since the previous discharge of curve 3.

We then allowed the battery to recharge up. And then we said, "Well what have we done to the battery? What did this discharge do to us?"

(Slide 105.)

I have on this graph shown (1) the initial curve I discussed in the first graph, after 1636 cycles, showing the degredation in discharge voltage. I have superimposed on that the rundown on a cyclic basis, showing how the battery discharge voltage -- how the pack discharge voltage was in fact decreasing.

So after we got this point, recharged, we went back after 15 cycles, allowing the battery to come up to full capacity. We then did a constant current discharge.

And the most significant fact that you could observe here is that until you approach the capacity at which

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you removed on the previous discharge you do in fact enhance the discharge voltage. But as soon as you pass through that approximate point that you have discharged the battery, the depth to which you have taken the battery previously, you are in fact down at the same voltage you would have had you continued that earlier discharge down.

(Slide 106.)

So we do that on ground testing. What happens in real life?

What I have attempted to show here, taking the OAO A-2 flight data, with the inputs of Mr. Harry Wasjgrass who works in the control center; which contributed significantly to this graph; I have plotted, or made an attempt to plot the battery discharge voltage and compare it with cell test data on the spare cells after 1636 cycles, which is the data we just reviewed.

Now you have to take into consideration here our accuracy from the flight telemetry data isn't anywhere near what we're doing on ground. So even though we have ampere hour integrators in the spacecraft on each battery, when you only have 10 minutes out of 100 minutes to be in contact with the spacecraft, you're never quite sure where you are at any given time.

So there could be an error of at least a half an ampere hour in any one of these points shown here.

wb24

But what I did show here is the fact that after the flight data, after 5625 cycles, or orbits, we are indeed retracing a similar curve. You begin to notice, and, if you care to extrapolate battery data, you would predict that this data would begin to fall down below this.

Now you might notice that this scale is greatly expanded from the previous scale, because on the cell discharge data we never see the low plateau. And in the operation of the battery in the spacecraft, the system was so designed such that they could not tolerate a buss voltage to operate on the lower plateau.

That's the point I'm making today: design your system to operate within the capabilities of the batteries that we're using today.

So you see that I also have flight data for Orbit 11,176. Now there's something interesting that comes out of all this when you begin to look at many, many orbits of data. Every time you run a deep discharge you do, in fact, erase some of the previous history. You only erase it to the point at which you run that discharge.

We begin to look at little bit further at this in later tests, and we begin to say "Well, when we look at the double plateau, how is that changing with cycle life?" So we set up a test on some subsequent cells, this is flight cells from batteries numbers 32 and 33, which Joe mentioned

wb25

earlier. We tried to evaluate what is happening at the inflection point. --and by "inflection point" I have, for reasons unknown to me at this point, identified 115 volts as a convenient factor of determining when I am in the transition period from the upper to the lower plateau.

Now what I have shown here is four cells. All cells had received 5717 cycles at this point. Cells 4 and 5 had been discharged completely at 2565 cycles. They had all been operated in a series string, or in the same test pack, same test condition. So, in effect, we have 5700 total cycles on all the cells; cells 4 and 5 had been discharged completely down to .5 volt -- which is my definition of "completely" in this case; and supposedly we had erased the effect of the previous cycling.

So then we begin to look. Okay: cell 2 certainly has a lower discharge voltage, and it's a lower plateau. And then we find Cell 3 and Cell4 and Cell 5. As luck would have it, Cell 3 did happen to fall pretty close to Cells 4 and 5.

What I have surmised from this is that the degredation as a function of cycle life is one that is probably asymptotic. This lower plateau approaches your depth of discharge asymptotically; being at a faster rate in early life than it is in later life. In other words, as you approach the depth of discharge the plateau moves in on

wb26

you at a much lower rate.

I'm sure you're sitting there and saying, "Well that's a bunch of bull."

What I would like to address myself to at this time is, let's look at the cell as an energy storage device, not as an ampere hour storage device. And I'm not so sure this can be read from the back of the room; but when we begin to look at the cell as an energy storage device it becomes quite interesting. Because what you're finding out is that you are getting a degradation in the watt-hour storage capability with life.

What I have plotted here is the discharge voltage of a cell early in life versus the watt hours for that pack, or at least the watt hours per cell, in this case. And for those who can't read this, this is 20, 40, 60, 80, 100, 120, 140 watt hours. And this is cell voltage, 1.3, 1.2 and 1.1. The dotted line represents the depth of discharge in ampere hours, which is 15 percent.

The percent capacity obtained on discharge is after 2345 cycles. So what we find here is that, while we have a degredation in the discharge voltage plateau, the watt hours to 1 volt is essentially the same. The ampere hours is not.

In order to maintain the watt hours the same it's obvious you're talking about a delta difference in the area of

C.S.

wb27

this curve. In order for the watt hours of this curve, of this discharge, to be the same as the watt hours for the others, the ampere hour capacity has to be slightly greater.

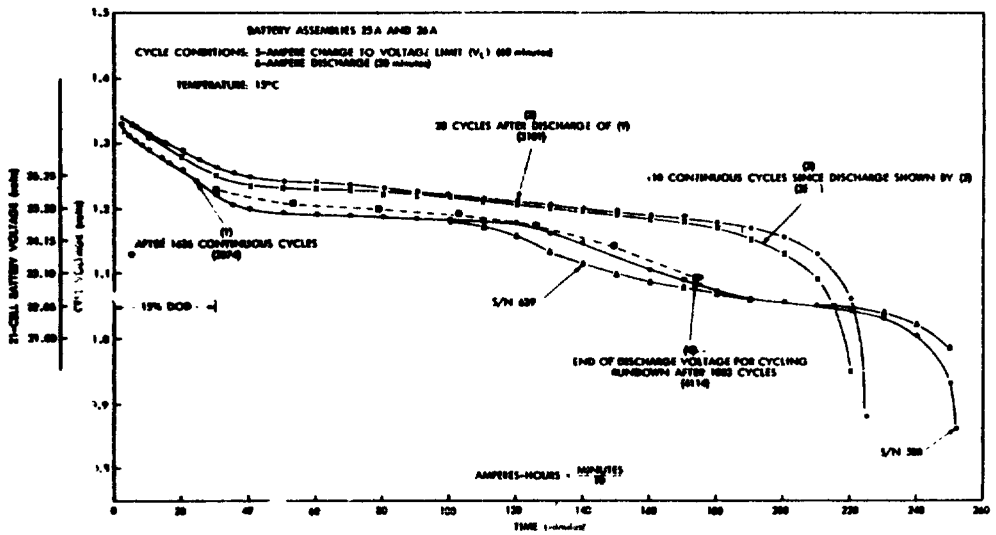
Okay. I've only showed you data for a few thousand cycles. In order to support this type of thinking, we initiated a test at Crane a little over two years ago. And as you know, as you're all probably familiar with, most of the Crane tests are discharged every eighty-eight days. So we decided we had better take a look and see what happens after two years without a discharge. Let's just cycle the battery for two years.

(Slide 107.)

And what I have plotted here is the watt hours at the various points, the test conditions that we took on those cells. This is the average watt hours per cell of a five-cell pack.

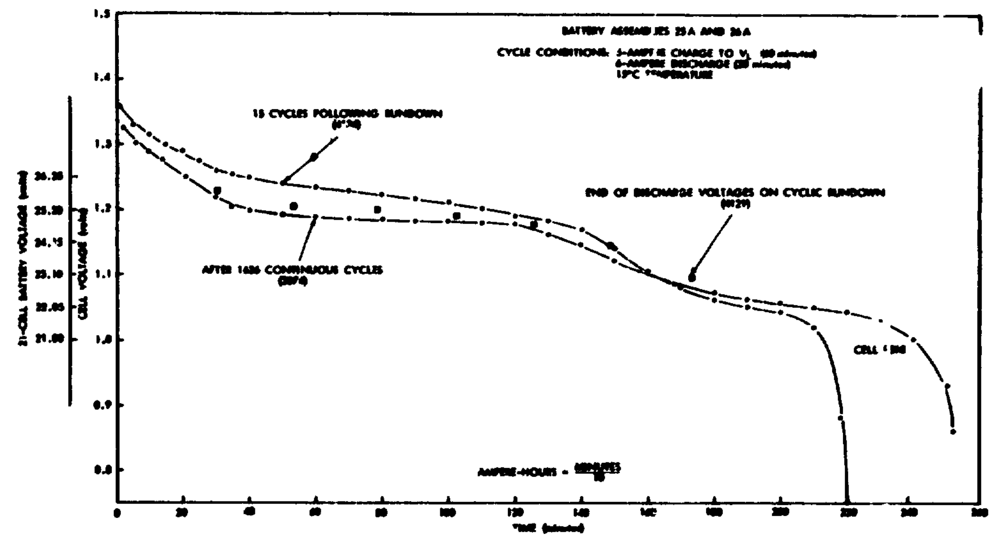
The upper curve is the pre-cycling data, run prior to cycling at the 1.8 ampere hour rate, which happens to be the rate to get a 15 percent depth of discharge on a 90-minute orbit.

After approximately 11,700 cycles you see that your discharge voltage is down. And something very impressive here is the fact that-- For those of you in the back who can't see, this is 1 volt, 1.1. The plateau in here is about 106 volts per cell. There's not a spacecraft flying today that can use that type of voltage on the unregulated



Voltage Profile for 6-Ampere Discharge After Various Numbers of Consecutive Cycles

Figure 104



Voltage Profile for 6-Ampere Discharge, Showing the Effect of Continuous Cycling

Figure 105

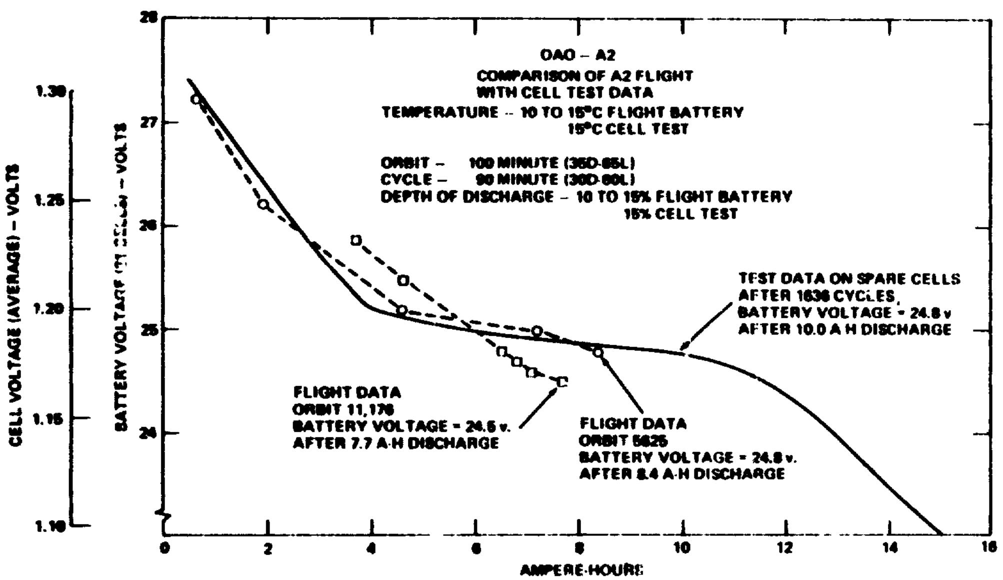


Figure 106

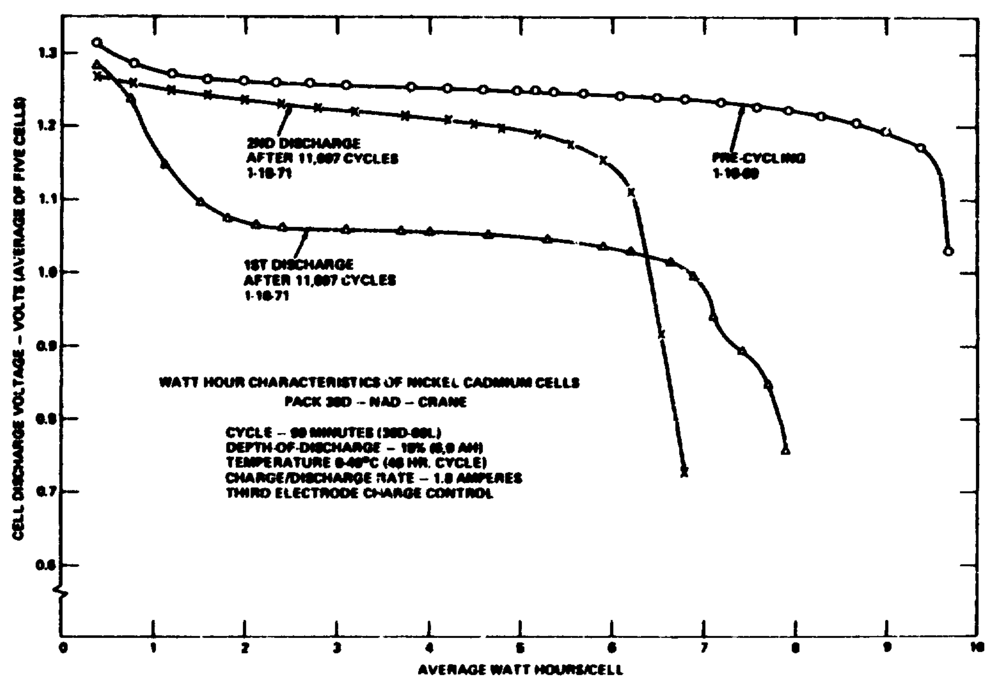


Figure 107

wb28

buss.

After the first discharge following the two-year cycling we recharged at the cycling rate, and ran a subsequent discharge.

You see you have in fact significantly improved the discharge voltage. But you did not improve the watt hour storage capability of that cell. My contention is that it has degraded, and that it's a rear, irreversible degradation at any point in life.

So what this sums up is that, while the watt hour capacity, or watt hour storage capability of a cell does degrade with life, the watt hours stored in that cell at any particular point in life is essentially the same. You can get it out at a lower voltage, a slightly higher capacity, or you can get it out at a higher voltage or a lower ampere hour capacity.

From a system viewpoint, the spacecraft designers don't like that lower curve.

What's the alternative?

The alternative is a recondition in space. That, in my estimation, is a gamble, a very wide gamble. Because when you look at the individual cell voltage data that generated these curves, we find out that on this discharge, as we went around the knee -- which is approximately 1 volt -- we had very uniform cell voltages. They all came down very close.

wb29

We recharge, and on subsequent discharge we had over -- we had one cell to fail the pack when the other cells were above 1 volt.

Essentially what happened, the cell voltage divergence, near the end of discharge, increased on the last capacity check.

These cells have completed two years. They were subsequently put back on cycling for another two years. What we're interested in generatingessentially is, what is happening to this type of data over a long period of time.

I have other vu-graphs in other areas, but I would like to stop. It's getting late. I would like to open it for questions. And if anyone would like to go further into this we will do so. But I wouldn't want to keep you here against your will.

Jim?

DUNLOP: Jim Dunlop from Comsat.

I liked the presentation that you made, for a number of reasons, Floyd; one of them being that we have observed with cycling certainly a similar problem to the one that you're talking about, in that we do observe a voltage degradation.

The problem seems to be that you can recondition: we do that pretty regularly; but the effect of reconditioning is a temporary one. And the more you cycle, the more you cycle the more temporary the effect of reconditioning becomes.

So that it's really not an answer, a complete answer, particularly when you're running a synchronous satellite application when you may not have the capability of reconditioning in the middle of the eclipse season when you meed the most power.

I would like to say just one thing in general.

We locked at your argument pretty carefully, too. And we decided that, based on it, what we would say is the way to use a battery is to use a regulator with it, which is a constant power device. This is from a system point of view. That means a boost regulator, in essence; use a boost regulator with the battery, and this gives you a constant power device so that you don't limit yourself to a voltage or an ampere hour number, what you're limiting yourself is to whatever energy you can take out of that cell.

FORD: Yes, Jim, I agree. We feel that reconditioning is at the most a temporary effect, and that it is something that you run a terrific risk in space when you do this. There is certain data available to suggest that the older cells get the more prone they are to show it on these deep discharges. And when I say "deep discharges," all the way down.

This, again, has other risk factors involved.

THOMAS: Charlie Thomas, Chrysler.

wb31

Floyd, you described a Crane test during which you allowed deliberate rundown of the stated charge. This is basically the same as this, or very similar to this PPC charging method that we came up with.

The results that we have seen -- of course these are preliminary, and I don't wantto go too far in discussing them at this point. But our results, test result, so far pretty well bear out what you have seen, that you do, by letting the stated charge vary -- the stated charge over which you operate, vary -- you do get improvement in the voltage characteristics. The basically the greatest improvement -- let's put it this way -- is in the range that you let the stated charge vary over. When you get outside of that range it appears that you don't have any improvement, or less improvement: let's put it that way.

FORD: Yes.

For the benefit of those people sitting here, we learned to live with this. We'd like to know that we don't have to live with it, because it does impose some additional restrictions from a design viewpoint, to design your discharge regulator to operate over a wider input voltage range throughout the life.

I would like to make one comment. I'm not sure Gerry is going to go into this tomorrow; but on the one type that I showed, which was OAO Pack 3, that had completed

wb32

approximately 6600 cycles, one cell is that pack has never been discharged, and we are, through the cooperation of Gerry Halpert's group, the Materials Section, making an attempt to analyze those cells. And I will not go into the details of what the analysis will be; but the objective is to try to identify what is the mechanism that is causing this. Is it the negative electrode? Is it the positive electrode?

I have my own feelings about that, but I will not present them here.

Any more questions?

Dean?

MAURER: Maurer, Bell Laboratories.

Might I suggest that you use the old trick of the lead acid plants in the telephone central offices and use so-called "N" cells and just switch in a few extra cells near the end of your discharge when the voltage drops too far.

FORD: A great idea. Convince the spacecraft manager to do that and you've overcome one of our problems.

(Laughter)

Are there other questions?

KRAUSE: Krause, JPL.

We've been running Mariner 71 batteries and cells in the lab for a couple of years now. And, of course, our cyclic requirements are considerably less for that type of

wb33

mission than you have for an earth orbital mission. But we've been running some cells at depth of discharge above 50 percent at around 15°C. and some at 94 percent of their rated 20-amp-hour capacity at that same temperature. And we've got about 250 cycles on the 94 percent cells, and six or seven hundred cycles on the one slightly over 50 percent.

We don't see at those depths of discharge and at 15°C. temperature, we don't see any real significant drop in the end of discharge voltages, nor have we seen any significant changes in the end of charge voltages with those cycle numbers and at that depth of discharge.

One might conjecture that the deeper depths of discharge may act as a self-reconditioning thing, up to a point.

As I say, we do run higher depths of discharge than most of the earth orbital satellites. but our lifetime requirements are considerably shorter.

I don't know what the effect of these deep depths of discharge will be eventually if we get above 1000 cycles. Obviously it will -- or probably it will foreshorten the overall life.

But we don't seem to see this double plateau, nor do we see any real significant fall off in voltage over many hundreds of cycles without reconditioning.

FORD: What cycle regime are you running these in?

wb34

You mentioned 90 percent. But what time?

THOMAS: We're running a 12-hour orbit on the ones at around 50 percent, and the 33-hour orbit on the ones at 94 percent. So, again, Ithink we're stressing the cells considerably less. We're charging at fairly low rates, like C/10.

FORD: The only comment I would like to make to that, Stan, is that there is a point in depth of discharge -- in fact maybe depth of discharge is the wrong number; maybe we should be talking about current density. This is something I think we've gotten a handle on that we've used as a crib, really, all our lives, or ever since we've worked with batteries. But maybe we're not using the right numbers.

I am definitely convinced in the area of capacity, capacity degredation, ampere hours isn't the right number. Watt hours is what we have to be looking at.

Now you talk about depth of discharge in the range of 60 to 90 percent. If you look at the Crane test data on synchronous orbit there are some very surprising things that come out of that data. By the simple fact than when you run cells on a synchronous orbit at high depths and low temperature, you almost invariably see a tremendous increase in cell capacity in the first year and a half. For example, some G.E. 12-ampere-hour cells rated, they delivered 15 ampere hours at the cycling rate before they started the

wb35

real time eclipse. In three eclipses these cells were up to 19 ampere hours.

Now some people look at that data and say that's good. I look at that data and say that's bad. Because I don't like it. I'd rather seen it go the other way, not by the same percent.

But when I see the positive plate capacity increasing, I start wondering what's happening to the negative late. If I knew it was increasing by the same percentage, that's good. But we don't have any data that says that's happening; in fact, it's contrary.

THOMAS: That's a good point.

One further comment is that our power system on all of our JPL spacecraft use a constant power system with a boost regulator. So our system can operate with the Mariner 71 down to 1 volt per cell. If we have to, we could operate on that lower plateau. But we haven't had to yet. We haven't seen it..

FORD: Well, we're with you there. All our new systems will be able to operate down to 1 volt per cell.

I believe Jim had a comment. But, Jim, could Dr. Shair comment, please?

SHAIR: Bob Shair, Motorola.

When you say the capacity went up in this polar orbit -- or I presume it was the 22-hour orbit, the 2 -hour

wb36

orbit, was not the cell sitting on overcharge for a long time in between its deep discharges; which we have some indication does increase the capacity.

FORD: Yes. Your statement is correct. These cells are on a 2-eclipse season per year, which is approximately 42 days. But to contrast that data you look at the other packs at different depths, and at different temperatures and the same depth. You don't see the same percentage increase.

The increase in ampere hour capacity is most predominant at the deep depth and at the cold temperatures, like 0°C.

Jim?

DUNLOP: Jim Dunlop, Comsat.

I would like to make a comment again on our results. And they don't agree with yours completely, Floyd.

We have never seen a loss in ampere hour capacity, period, in all of our cycling. We have seen a slight increase. And we attribute that increase in ampere hour capacity-- UnfortunatelyI think one of the problems with the kind of thing we're discussing right now is, you're talking about one cyclic regime, I'm talking about another cyclic regime, Bob Shair is talking about another cyclic regime, the people at JPL are talking about another cyclic regime. And to make completely general conclusions based on any set of test data to cover all conditions I find to be one of the major frustrating problems I encounter in trying to design a battery for a synchronous satellite. And I'm convinced that my data is right, because I run it like we run a synchronous satellite.

(Laughter)

FORD: I'm glad you brought that point up, Jim, because I want to clarify that.

I didn't say the ampere hour capacity did not degrade with life. As with the watt hour capacity, it does degrade with life.

DUNLOP: I said mine didn't.

FORD: Okay.

If you look at the Crane test data, in a year and a half or two years, those cells don't either.

DUNLOP: I'm up to three.

FORD: Just to illustrate this point, what I've plotted here -- and, again, it's not coming out that clear -- is percent of rated capacity, which is 6 ampere hour cells. These happen to be Gulton cells, and they're using third electrode charge control. This is at zero volts, half a volt, and 1 volt.

(Slide 108.)

And what I compared here was two packs -- I didn't show data on the 25 percent depth, but we have the same type

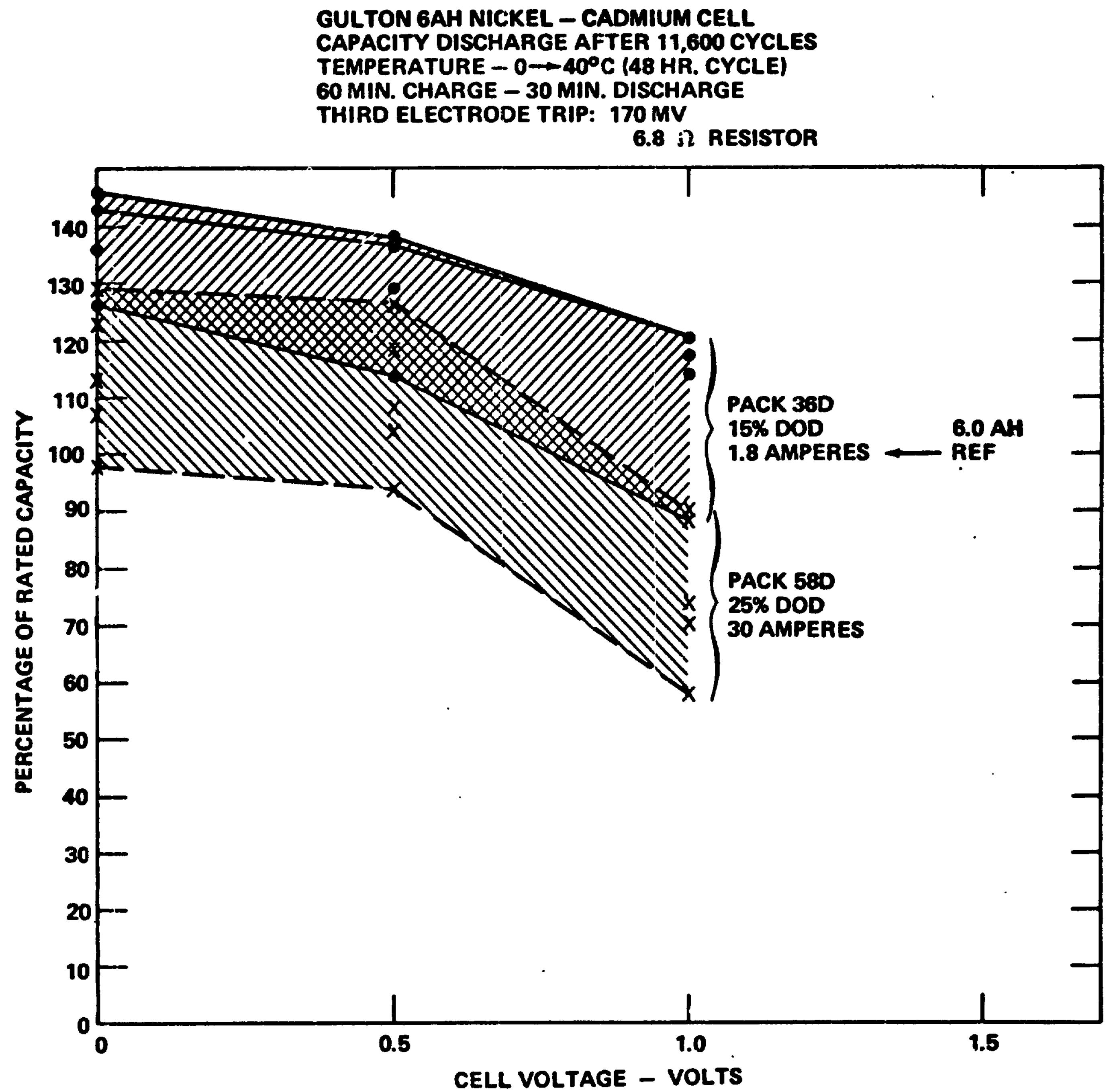

GULTON 6AH NICKEL – CADMIUM CELL
CAPACITY DISCHARGE AFTER 11,600 CYCLES
TEMPERATURE – 0⟶40°C (48 HR. CYCLE)
60 MIN. CHARGE – 30 MIN. DISCHARGE
THIRD ELECTRODE TRIP: 170 MV
6.8 Ω RESISTOR
PERCENTAGE OF RATED CAPACITY
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
0
0.5
1.0
1.5
CELL VOLTAGE – VOLTS
PACK 36D
15% DOD
1.8 AMPERES
6.0 AH
REF
PACK 58D
25% DOD
30 AMPERES

Figure 108

wb38

of data on the 25 percent depth. And it definitely proves that the degradation in ampere hours and watt hours is related to depth of discharge.

This is nothing new. We've always expected that, or known it, in fact.

What I attempted to show here is to show with a spread of five cells for the pack at 25 percent depth at the 1 volt point, the half volt point. And here is 100 percent, which is 6-ampere-hour cells here. These cells, we knew, deliver approximately 112 percent of rated cells, so in these cells will deliver capacity here.

Now if you look at the capacity to 1 volt you find out that they have indeed lost capacity.

And one point I would like to make here that I don't think we can pass off too lightly: when comparing cells at a cycle at 15 percent depth of discharge with those at 25 percent depth of discharge you find a larger percentage of your capacity below 1 volt and even below a half volt at 25 percent than you do at 15 percent.

I can't separate this type of data from the overall observation of this degradation in discharge voltage above 1 volt. It's all tied together.

Again, it relates back to the cell is truly an energy storage device, so you have to remove all the energy to find out what the degradation is. When we discharge a

wb39

cell to 1 volt we don't remove all the energy.

(Slide off)

Bob Steinhauer.

STEINHAUER: Bob Steinhauer, Hughes.

With regard to the higher depths of discharge, 60 percent and on deeper, at least in the 60 to 70 percent, I think if you're really looking for the double plateau keep cycling.

Second, I don't know what's going to happen at the very high depths. The rate of onset seems to be slower, but it does occur.

We do, incidentally, have satellites flying that do boost,regulate on discharge. And this does seem to be an approach that would work. But I think we still should find out the mechanism of this double plateau.

FORD: Jim?

DUNLOP: One comment with respect to what he just said.

He said we ought to find out the mechanism. And I agree. And I want to make a little pitch right now.

I think if you want to find out what is going on in these cells, and you base everything you see just on your electrochemical measurements, that you get half the story.

Last year Wright-Patterson, through some of the efforts with Dr. Fleischer, Comsat, Goddard, have been doing

wb40

a lot of work to try and add to their body of data a complete analysis of that cell. And I mean a complete analysis of the state of charge of the material-- If you're talking about a loss in ampere hour capacity in a positive or a negative plate you should know, if you're going to complete your story you should know whether you're talking about a loss in ampere hour capacity because you've got charged material you can't discharge, you've got discharged material you can't charge, you're changing the utilization, you've got higher valence states that you can't discharge, or something else: but just to make these kinds of statements, and unfortunately -- and conclusions based only on these electrochemical measurements, sometimes tends to confuse more than answer questions.

I think what everybody would like to see is some good answers. And I think that many people, including Goddard, have been working very hard in the last couple of years to try and find out these answers through more detailed analysis of that cell.

FORD: I agree, Jim. Thank you.

Do we have any other questions before we adjourn at five minutes till six?

We're making it by six.

Okay. I'd like to thank you for coming. And I believe the meeting will re-adjourn in the morning at nine

wb41

o'clock, in the same room, but with different people.

Okay. Thank you.

(Whereupon, at 5:55 p.m., the meeting was adjourned.)

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